Dielectric and Fluorescent Probes To Investigate Glass Transition, Melt, and Crystallization in Polyolefins

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ABSTRACT: Investigation of glass transition dynamics in polyolefins by broadband dielectric spectroscopy (DRS) is facilitated by the addition of a novel dielectric probe, (4,4'-(N,N-dibutylamino)-(E)-nitrostilbene (DBANS), which introduces dipoles and made the polymers dielectrically active. For probe concentrations between 0.1% and 1.0% the dielectric strength  $\Delta \epsilon$  associated with the dynamic glass transition increases proportionally to the probe concentration. This result indicates that the probe exhibits no intramolecular relaxations, and the probe rotational diffusion effectively senses the "microviscosity" of the probe environment on the length scale of the segmental dynamics. Temperature-dependent fluorescence spectroscopy on doped polymers shows no changes in fluorescence wavelength around the glass transition temperature. Crystallization and melting of the polyolefin matrix results in an increase or decrease of the probe concentration in the amorphous phase, which was clearly detected by real-time fluorescence because the probe emission is sensitive to the probe content, particularly at higher probe concentrations.

## Introduction

In the past decades broadband dielectric spectroscopy (DRS) has been widely used for the study of molecular dynamics in many liquids and polymers because of its dynamic range of more than 15 decades in frequency.<sup>1–4</sup> As it is an experimental technique that probes fluctuations of molecular dipoles and translational diffusion of charged particles, DRS allows the study of molecular motions on various length scales ranging from individual bond rotations, the cooperative glass transition up to the relaxation dynamics of entire polymer molecules. Since DRS spans a wide frequency range (>8 decades for standard dielectric instrumentation) and can easily be performed at different temperatures, this technique provides a wealth of information on molecular dynamics.

Typical examples of polymers studied by DRS include traditional amorphous (PMMA) and semicrystalline-polymers (PET, PEN, PEO),<sup>2,5,6</sup> complex, (multiphase) liquid-crystalline polymers,<sup>7,8</sup> and nanocomposites or supramolecular polymers.<sup>9</sup>

A prerequisite for the application of dielectric relaxation spectroscopy is the presence of dipoles, which provide the necessary link between the molecular motions and the interactions with an external electrical (probing) field. Though most of the polymer systems contain at least weakly polar groups, in either the main chain or the side chain, there is a substantial class of nonpolar polymers like polyolefins, which do not have dipoles. To overcome this problem, various methods that aim to introduce permanent dipoles have been proposed. A few of them will be discussed briefly.

Relaxation phenomena in polyethylene have been the subject of extensive dielectric studies since the early days of DRS.<sup>6</sup> To introduce polar groups, either oxidation (the introduction of a carbonyl functionality) or chlorination of the polymer chain has been used.<sup>10</sup> A recent improvement of the oxidation strategy was the introduction of titanium dioxide<sup>11</sup> as an oxidation catalyst, which enables good control over the degree of

oxidation without appreciable change in crystallinity. It is generally assumed that introduction of a small number of carbonyl or chlorine groups does not affect the molecular motions in polyethylene. The polymer is merely decorated with dipoles, which serve as dielectrically active labels. The molecular origins of relaxation phenomena in (modified) polyethylenes are well understood.<sup>12,13</sup> The crystalline  $\alpha$  relaxation is connected to the longitudinal helical motion of chains through the crystal lamellae (rotator phase). This motion forces the decorating dipoles to move through a number of translational and rotational steps, which suffices for dielectric activity. The  $\beta$  relaxation, the next process in sequence proceeding toward lower temperatures, is associated with the dynamic glass transition in the amorphous regions as indicated by the temperature dependence of its relaxation time  $\tau_{\beta}(T)$  according to the Vogel–Fulcher– Tammann law.<sup>14–16</sup> At even lower temperature, the  $\gamma$ relaxation can be observed the nature of which was assigned to a local sub- $T_{\rm g}$  kink inversion process in the amorphous regions of polyethylene.

For isotactic polypropylene (*i*·PP), dielectric spectroscopy is less commonly used as a characterization tool. Although oxidation will introduce dipoles into the material, it will also lead to chain scission,<sup>17</sup> with obvious consequences for the molecular weight of the polymer. For other polyolefins, similar limitations apply, and the introduction of dipoles without affecting the overall polymer properties is difficult.

In this paper we propose an alternative method to introduce polar groups in apolar polymers: addition of a highly polar "dielectric probe". For this purpose we have chosen a rigid-rod-type molecule, 4,4'-(N,N-dibutylamino)-(*E*)-nitrostilbene (DBANS), which fulfills various requirements: (i) the molecule is rigid which eliminates dielectric relaxations associated with intramolecular motions, (ii) the probe has a large permanent dipole moment (9 D),<sup>18</sup> and (iii) the molecule has sufficient solubility in an aliphatic environment due to the presence of the butyl tails, which also reduces the

tendency of the probe to crystallize. Probes have been used for considerable time to monitor combined motions of a guest with a host medium.<sup>19</sup> It has been shown dipolar probes can be used to monitor reorientational motions, for example in *o*-terphenyl.<sup>20–23</sup> More recently, fluorescent probes were used by Thurau et al. to study physical aging by monitoring both rotational and translational diffusion of dye molecules in polymer matrices.<sup>24-26</sup> Plasticizer/polymer interactions have been studied in the 1970s.<sup>27</sup> For polystyrene these studies revealed that at low concentrations partial motions of the plasticizer molecules gave rise to a low-temperature relaxation. Residual orientational degrees of freedom of the plasticizer activated at the dynamic glass transition yielded further an enhancement of the dielectric  $\alpha$ -process of polystyrene.

The aim of the present work is twofold: first, we intend to show the capabilities of the dielectric probe approach as a generic technique to sensitize apolar polymers for dielectric spectroscopy investigations. For this purpose we have studied three different polymers, low-density polyethylene (LDPE), isotactic polypropylene (*i*-PP), and atactic polystyrene (PS), which have been doped with DBANS in concentrations between 0.1 and 1%.<sup>28</sup> Since the latter polymer (PS) shows a weak polarity due to the small dipole moment of the styrene groups, polystyrene is used as a reference material that allows a direct comparison between the dielectric relaxations of the undoped polymer with that of the doped polymer.

The second aim of this work is to use DBANS as fluorescent probe. Charge transfer probes, like (dialkylamino)nitrostilbene derivatives, have been used extensively as fluorescent probes for monitoring polymerization processes and polymer characterization.<sup>29–37</sup> Temperature-dependent emission is recorded in order to find out how the probe fluorescence is related to polymer dynamics. This will reveal to what extent dielectric response and fluorescence response provide equivalent or complementary information on the changes in the polymer mobility, particularly at the glass transition or during melting/crystallization.

## **Experimental Section**

**Sample Preparation.** The polymers were received from Shell (PS, Shell N7000,  $M_w = 371\ 000\ M_w/M_n = 3.3$ ) and Sabic Stamylan (LDPE, Sabic 2100TN00, MFI 0.3; *i*-PP, Sabic 11E10, MFI 0.3). Polystyrene was purified by a triple precipitation from dichloromethane/methanol. *i*-PP and PE were used as received.

Mixtures of polymer with DBANS were prepared by melt mixing in a 20 cm<sup>3</sup> Brabender batch mixer at 200 °C. Thin sheets of doped polymer were prepared by hot pressing using 0.3 mm aluminum spacers and were used for fluorescence, DSC, and DMA measurements. From these sheets square pieces of 1 cm<sup>2</sup> were cut and pressed together with 100  $\mu$ m glass fiber spacers between circular brass electrodes (diameter = 2 cm), resulting in samples with a well-defined geometry for DRS experiments.

**Dielectric Relaxation Spectroscopy.** Dielectric experiments were performed using a high-precision dielectric analyzer (ALPHA analyzer, Novocontrol) in combination with a Novocontrol Quatro temperature system providing control of the sample temperature with an accuracy better than 50 mK. All dielectric measurements were performed in the frequency range from  $10^{-1}$  to  $10^7$  Hz. Temperature-dependent experiments were realized by consecutive isothermal frequency sweeps in the temperature range from +200 to -120 °C in steps of -5 K, which resulted in an effective cooling rate of

about 0.5 K/min. More experimental details can be found in ref 5.

To determine the relaxation time  $\tau(T)$  from the dielectric loss curves, we have fitted the frequency spectra  $\epsilon''(\omega)$  by the empirical Havriliak–Negami relaxation function (eq 1) using the Levenberg–Marquardt algorithm:<sup>38,39</sup>

$$\epsilon'' = -\mathrm{Im}\left\{\frac{\Delta\epsilon}{\left(1 + (i\omega\tau)^a\right)^b}\right\} + \frac{\sigma}{\epsilon_0\omega} \tag{1}$$

Here  $\Delta \epsilon$  and  $\tau$  correspond to the relaxation strength and the mean relaxation time of the relaxation process. The two shape parameters *a* and *b*, which determine the logarithmic slope of the low-frequency loss tail *a* and the high-frequency loss tail -ab, are determined by the underlying distribution in relaxation times. The second term in eq 1 accounts for ohmic conduction.

**Differential Scanning Calorimetry.** DSC heat flow curves of all samples were recorded with a Perkin-Elmer DSC-7. Indium was used for temperature calibration. All samples were annealed for 5 min at 220 °C and subsequently cooled at a rate of 10 K/min. Glass transition temperatures were determined from the  $C_p$  inflection point via differentiation.

**Dynamic Mechanical Analysis (DMA).** DMA measurements were done on a Perkin-Elmer DMA-7 instrument in tensile mode at 1 Hz. Samples were heated with a rate of 5 K/min.

**Optical Microscopy.** Optical microscopy was done with a Nikon Eclipse E600-POL microscope fitted with a Mettler FP82 HT hot stage and a Nikon coolpix 4500 digital camera. *i*-PP samples containing 1% DBANS probe were repeatedly heated to 200 °C and cooled at a rate of 10 K/min to 50 °C.

**Fluorescence Spectroscopy.** Fluorescence spectra were recorded with a Spex/Jobin-Yvon Fluorlog 3 fluorescence spectrometer equipped with a fiber-optic cable in combination with a Linkam hot stage, which was kept under a stream of dry nitrogen during the experiments. Temperature-dependent measurements were carried out isothermally in steps of 10 K in cooling from +150 to -100 °C at 10 °C/min. Fluorescence experiments using DBANS were carried out with an excitation wavelength of 400 nm. The angle of the incident beam was kept at 45° to the plane of the sample in order to minimize back-reflection of excitation light. The emission spectra, corrected for the wavelength-dependent sensitivity of the photomultiplier tube, were recorded with wavelength intervals of 1 nm.

Real-time fluorescence was recorded on an SGL/Oriel CM1000 cure monitor.<sup>40</sup> Freshly prepared samples were heated to 190 °C at the chosen heating rate, held at 190 °C for 5 min and subsequently cooled to 30 °C.

**Synthesis.** TLC analysis was performed on silica gel (Merck, F254); <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured at 300 MHz (Varian Unity Inova spectrometer) or 400 MHz (Varian VXR 400S spectrometer). <sup>1</sup>H chemical shifts are given in ppm ( $\delta$ ) relative to tetramethylsilane (TMS) as internal standard. Toluene was dried by refluxing with sodium for 6 h and then purified by subsequent distillation.

(4-Nitrobenzyl)phosphonic Acid Diethyl Ester (2). 4-Nitrobenzyl bromide (10 g, 46.3 mmol) in triethyl phosphite (8.46 g, 50.9 mmol) was transferred to a three-necked round-bottom flask of 250 mL and fitted with a cooler and a gas inlet fitting. Then the mixture was gradually heated to 80 °C under a continuous stream of nitrogen. After stirring for 4 h at this temperature, the mixture was allowed to cool to room temperature. The mixture was coevaporated with water (2 × 50 mL) and dry toluene (2 × 50 mL). The resulting brown oil (12.5 g, 99%) was used in the next step without further purification.

4-(Dibutylamino)benzaldehyde (4). To a solution of 4-fluorobenzaldehyde (11.57 g, 93. mmol) and dibutylamine (23.6 mL, 140 mmol) in DMSO (120 mL) was added dry potassium carbonate (13 g, 93 mmol). The solution was then sonicated for 15 min and subsequently heated to 100 °C for 48 h under vigorous stirring. The solution was then poured into water (500 mL) and extracted with ether (3  $\times$  100 mL). The combined



organic layers were washed with water (2  $\times$  200 mL), dried (MgSO<sub>4</sub>), and concentrated in vacuo to a yellow oil. Unreacted 4-fluorobenzaldehyde and dibutylamine were removed by coevaporation with water (2  $\times$  100 mL) and toluene (2  $\times$  100 mL). The resulting 4-(dibutylamino)benzaldehyde (16.9 g, 78%) was sufficiently pure for use in the next step.

(E)-4-(Dibutylamino)-4'-nitrostilbene (5). To a solution of 2 (2 g 7.32 mmol) in dry DMF (50 mL), potassium tert-butoxide (0.82 g, 7.32 mmol) was added at room temperature. At this point the color of the solution changes from slightly yellow to dark purple. After 15 min, 4-(dibutylamino)benzaldehyde (1.54 g, 6.59 mmol) was added and stirring was continued for 24 h. The solution was then poured into water (500 mL) and extracted with ether (3  $\times$  100 mL). The combined organic layers were washed with water (2  $\times$  200 mL), dried (MgSO<sub>4</sub>), and concentrated in vacuo to a dark red oil, which was purified by recrystallization from methanol to give pure 5 as red platelets (2.33 g, 90%); mp = 114 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 0.97 (t, 6H, J = 7.6 Hz, CH<sub>3</sub>), 1.39 (m, 4H,  $\gamma$  CH<sub>2</sub>), 1.59 (m, 4H,  $\beta$  CH<sub>2</sub>), 3.30 (t, 4H, J = 8 Hz,  $\alpha$  CH<sub>2</sub>), 6.62 (d, 2H, J = 9.2Hz, 3-CH), 6.87 (d, 1H, J = 16 Hz, stilbene H), 7.18 (d, 1H, J = 16 Hz, stilbene H), 7.40 (d, 2H, J = 8.8 Hz, 2'-H), 7.53 (d, 2H, J = 8.4 Hz, 2-H), 8.15 (d, 2H, J = 8.8 Hz, 3' H).<sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 14.0 (CH<sub>3</sub>), 20.3 ( $\alpha$  CH<sub>2</sub>), 29.5 ( $\beta$  CH<sub>2</sub>), 50.77 (γ CH<sub>2</sub>), 111.5, 120.8, 123.2, 124.1, 125.9, 128.6, 133.8, 145.2, 145.7, 148.7 (C/CH stilbene system).

#### **Results and Discussion**

Synthesis. For the synthesis of (dialkylamino)nitrostilbene-based probes from substituted benzaldehydes very often a condensation of 4-nitrophenylacetic acid in piperidine is used.<sup>41</sup> However, this strategy has the disadvantage that, along with the desired reaction, 4-nitrophenylacetic acid decarboxylates spontaneously under the used reaction conditions. This means that only very reactive (dialkylamino)benzaldehydes will give reasonable yields. Moreover, formation of piperidine carbonate from the CO<sub>2</sub> released by the reaction causes clogging of the reflux condenser, making this procedure hazardous if performed on a larger scale. Therefore, we employed an alternative procedure using a Wittig-Horner reaction (see Scheme 1).<sup>42</sup> Condensation of 4-nitrobenzyl bromide (1) with triethyl phosphite gave the corresponding phosphonate **2** in quantitative yield. 4-(Dibutylamino)benzaldehyde (4) was prepared by nucleophilic substitution of the fluorine moiety from 4-fluorobenzaldehyde with dibutylamine, using a similar procedure published earlier by Lupo et al.43 Condensation of the deprotonated phosphonate with 4 gave stilbene 5 in 90% yield.

**Differential Scanning Calorimetry and Dynamic Mechanical Analysis.** Differential scanning calorimetry (DSC) is generally regarded as a convenient and reliable technique for measuring (apparent) phase transition temperatures. An alternative technique to detect phase "transitions" in polymers is dynamic mechanical analysis (DMA). Here DSC and DMA are employed as reference techniques to determine phase transition temperatures. The glass transition temperature is operationally defined as the inflection point in the DSC heat flow curve at a cooling rate of 10 °C/min.<sup>44</sup> For DMA the maximum in the loss modulus is defined as the operational glass transition temperature.

In addition, DSC is used to investigate whether addition of probe affects the phase transitions and also to determine the degree of crystallinity of the polyolefins.

The DSC curves recorded for all LDPE samples, containing 0, 0.1, 0.5, and 1.0% probe, are identical within experimental error. The expected  $c_p$  steps at -120 and -35 °C, usually assigned to a sub- $T_g$  relaxation and the calorimetric glass transition, were not detected using standard DSC conditions.<sup>45</sup> The melt and crystallization peaks are observed at 109 and 92 °C, respectively, and from the crystallization enthalpy a degree of crystallinity of about 25% was determined. From the DMA loss curve, a  $T_g$  value of -31 °C was found for undoped LDPE.

From the DSC curves of the *i*-PP samples, containing 0, 0.1, 0.5, and 1.0% probe, a vague pseudo-second-order type transition is visible around -8 °C. Crystallization enthalpies are similar for all samples, and the degree of crystallinity is around 40%. The crystallization temperatures of *i*-PP vary between 106 and 111 °C, but no correlation between the crystallization temperature  $T_c$  and the concentration of DBANS is found. From the DMA loss curve maximum the  $T_g$  (f = 1 Hz) of undoped *i*-PP was determined to be around -8 °C.

DSC measurements on the PS samples showed a clear  $c_{\rm p}$  step at about 96 °C, which gradually shifts to lower temperatures as the probe contents increases. DMA measurements performed on undoped PS revealed a  $T_{\rm g}$  at 93 °C.

Crystallization enthalpies  $\Delta H_c$  have been determined for LDPE and i-PP and from them degrees of crystallinity are calculated. Accurate determinations of  $\Delta H_c$ were only obtained for *i*-PP because of extensive tailing of the crystallization exotherm of LDPE. Glass transitions for LDPE were not detected by DSC, and therefore the effect of probe addition on the calorimetric response is not known.

From the results summarized in Table 1, a number of conclusions are drawn. The crystallization temperatures of LDPE are all the same within experimental

 Table 1. Phase Transition Temperatures and Enthalpies

 Determined by DSC and DMA

			DSC					
polymer	C <sub>probe</sub> [%]	<i>T</i> g <sup><i>a</i></sup> [°C]	<i>T</i> c <sup><i>b</i></sup> [°C]	<i>T</i> m <sup><i>b</i></sup> [°C]	$\Delta H_{\mathrm{cryst}}^{c}$	$\frac{T_{g}^{d}}{[^{\circ}C]}$		
LDPE	0		92.1	109.2	-78.7	-31		
	0.1		92.3					
	0.5		92.6					
	1.0		92.8	108.7	-77.4			
<i>i</i> -PP	0	-5.6	106.6	160.9	-88.5	-9		
	0.1	-4.3	110.8					
	0.5	-5.4	107.6					
	1.0	-5.6	106.6	160.4	-86.8			
PS	0	99.5				93		
	0.1	98.0						
	0.5	96.1						
	1.0	93.6						

<sup>*a*</sup> Determined from inflection point. <sup>*b*</sup> Heating/cooling rate 10 °C/ min. <sup>*c*</sup> In J/g. <sup>*d*</sup> Mechanical loss (*E'*) peak maximum at 1 Hz.



**Figure 1.** Dielectric constant  $\epsilon'$  of undoped LDPE and LDPE/ DBANS blends at f = 13 kHz as a function of temperature. For a better comparison, all curves have been fine-tuned to the permittivity of undoped LDPE (0%) at -20 °C.

error, 92.5  $\pm 0.4$  °C. Crystallization enthalpies show similar values for all samples, indicating a degree of crystallization around 25%. The crystallization temperatures of *i*-PP vary between 106 and 111 °C, which might indicate the presence of nucleating agents. However, since the deviations are random, it is unlikely that the probe acts as nucleating agent, an idea that is supported by the observation that no significant influence of the probe content on the degree of crystallinity (~40%) was found. For LDPE and *i*-PP, glass transitions could not be determined for different concentrations of DBANS. In PS, however,  $T_{\rm g}$  values drop by 6 °C as 1% of probe is added to the polymer, indicating a slight but significant plasticizing effect of the probe molecule. Melting or crystallization of the probe itself around 114 °C has not been observed in any sample.

**Dielectric Relaxation Spectroscopy.** Thermal Transitions Observed in the Real Part  $\epsilon'(T)$  of the Complex Permittivity. A typical result from the DRS experiments is shown in Figure 1, which gives the temperature dependence of the dielectric constant  $\epsilon'$  at 13 kHz for LDPE samples at different probe concentrations, measured during cooling. These graphs reveal a number of characteristic features:

(i) At about 100 °C, a sharp step in the permittivity shows up as a common feature for all curves, accompanied by a change in the slope  $d\epsilon'/dT$ . This discontinuity indicates fast crystallization of the LDPE samples and does not show any sensitivity to the probe concentration (c = 0, 0.1, 0.5 and 1.0% (m/m)).



**Figure 2.** Dielectric constant  $\epsilon'$  of undoped PS and PS/DBANS blends at f = 13 kHz as a function of temperature. For a better comparison, all curves have been fine-tuned to the permittivity of undoped PS (0%) at 0 °C.

(ii) In the temperature range from about 30 to 0 °C, a drop in  $\epsilon'(T)$  is observed. We attribute this to the freezing of molecular dipoles upon passing the dynamic glass transition. The magnitude of which clearly relates to the concentration of DBANS probe molecules in the LDPE/DBANS mixtures.

(iii) Below  $T \sim 0$  °C the  $\epsilon'(T)$  curves are practically identical despite the differences in probe concentration from 0% (undoped LDPE) to 1.0% (m/m).

The apparent large change in permittivity in Figure 1 upon cooling can be attributed to the high viscosity of the LDPE (MFI 0.3), which led to an equilibrium thickness larger than the thickness of the spacers used, thus creating a situation where crystallization shrinkage leads to an apparently increased permittivity upon cooling. For *i*-PP, which is another representative example of a semicrystalline polyolefin, the same behavior has been found, although stronger deviations in the  $\epsilon'(T)$  curves between different samples and between heating and cooling runs were observed. These deviations are probably caused by a wide cold crystallization range and the generally far slower crystallization kinetics of *i*-PP compared to that of LDPE.

The corresponding  $\epsilon'(T)$  results of the third polymer, PS (cf. Figure 2), are in line with the previous results but show characteristic features typical for a fully amorphous polymer. Apart from the absence of a crystallization/melting transition, there is a pronounced kink in  $\epsilon'(T)$ , i.e., a change in slope ( $d\epsilon'/dT$ ), around 95 °C, a temperature which coincides well with the dilatometric glass transition. In other words, the dynamic glass transition in PS manifests itself in the DRS measurements in two ways: (a) by a discontinuity in the high-frequency ("optical") permittivity that is related to the density (of predominantly electronically polarizable species) and (b) by a dielectric relaxation related to the (im)mobilization of probe molecules, the position of which is frequency-dependent.

Specific Enhancement of the Primary Relaxation by Dielectric Probe Molecules. Let us now focus on the relaxation phenomena and the role of DBANS probes in more detail. For this purpose, we will discuss the dielectric loss curves  $\epsilon''(T)$  given in Figures 3–5 for LDPE, *i*-PP, and PS, respectively.

The isochronal representation of the dielectric loss, i.e.,  $\epsilon''(T)$  at a fixed frequency (f = 13 kHz), for LDPE samples with various concentrations of DBANS is shown in Figure 3. All four samples reveal the three principal relaxation processes known for LDPE, the  $\gamma$ ,



**Figure 3.** Dielectric loss  $\epsilon''(T)$  at f = 13 kHz for undoped LDPE and three LDPE/DBANS blends.



**Figure 4.** Temperature dependence of the dielectric loss  $\epsilon''$ -(T) at f = 13 kHz for undoped *i*-PP and three *i*-PP/DBANS blends.

 $\beta$ , and  $\alpha$  process. The clear detection of all three dielectric relaxations in the sample of undoped LDPE indicates a (natural) slight degree of oxidation of the polymer. It should be stressed that the order of the dielectric losses ranging from tan  $\delta = 10^{-4} - 10^{-3}$  must be regarded as extremely low and are only detectable with state-of-the-art high-resolution DRS analyzers (see Experimental Section).

Figure 3 further illustrates the effect of probe concentration on the dielectric relaxation behavior, particularly expressed by an increased strength of the  $\beta$ process, associated with the dynamic glass transition, while the strength of the  $\gamma$  process remains practically unaltered. Changes in the  $\alpha$ -relaxation that involves molecular motions of chain segments within or close to the crystalline lamellae do not show a clear trend because of the interference with ohmic conduction, interfacial relaxations (Maxwell–Wagner processes), and the vicinity of the dominant  $\beta$ -relaxation. Although minor effects of doping on the  $\alpha$ -relaxation cannot be excluded on the basis of the experimental data, it is obvious that the  $\alpha$ -process shows a much weaker, if any, sensitivity to the probe concentration than the  $\beta$ -process.

The effect of addition of DBANS to *i*-PP on the loss is completely analogous to that in LDPE as demonstrated in Figure 4. Here, again a selective "amplification" of the dielectric glass transition ( $\beta$ ) process is observed.

Finally, the doping effect on the loss tangent is demonstrated for PS, representing a fully amorphous polymer; the results are given in Figure 5. Again a systematic increase in the glass transition ( $\alpha$ ) peak intensity was found without any significant influence on the sub- $T_{\rm g}$   $\beta$  transition. It should be noted that



**Figure 5.** Dielectric loss tangent tan  $\delta(T)$  at f = 13 kHz for undoped PS and three PS/DBANS blends.

undoped PS, in contrast to the aliphatic polymers *i*-PP and LDPE, possesses a weak intrinsic dielectric glass transition signal relaxation, which originates from the residual dipole moment of the styrene group. Taking advantage of its intrinsic dielectric activity, PS gives us the unique opportunity to compare two different dielectric manifestations of the glass transition dynamics in the same material: (a) a direct one due the presence of intrinsic "markers" (the styrene dipoles) and (b) an indirect response caused by the coupling of probe molecules to the cooperative dynamics. Since there is no significant shift in the loss peak maximum temperature discernible in Figure 5, we must conclude that the probe dynamics is very closely related to the intrinsic glass transition dynamics, a fact that will be discussed in more detail in a following section.

The second important conclusion that can be drawn from Figures 3–5 is the strikingly selective sensitivity of the probe dynamics to the dynamic glass transition. This phenomenon can be rationalized by considering the length scale of the various relaxation processes with the relevant length of the probe molecule (the rigid core) being on the order of 1.5 nm. Since large angular fluctuations of the main molecular axis are a prerequisite for a strong dielectric response, only cooperative molecular motions on the scale of >2 nm are expected to allow large-amplitude angular fluctuations of the probe main axis. While the dynamic glass transition, for which typical length scales of the cooperativity on the order of 1-5 nm are discussed,<sup>46</sup> clearly fulfills this criterion, local processes such as the  $\gamma$ -relaxation in LDPE do not lead to large-scale rotational diffusion of the rigid probe axis due to the small length scale of molecular reorientation.

To explain the obvious weak sensitivity of the probe molecules to the crystalline  $\alpha$ -relaxation present in LDPE and *i*-PP, we have to recall the molecular assignment of the dielectric  $\alpha$ -process,<sup>47</sup> being an intracrystalline process that involves longitudinal diffusion of chain segments by a helical motion. Because of the high preference of the probe molecules to dissolve in the amorphous phase, it is unlikely that the DBANS molecules are efficiently coupled to the molecular motions involved in the  $\alpha$ -relaxation.

Concentration Dependence of the Dielectric Response. To discuss the impact of the probe concentration on the intensity of the dielectric glass transition process, we have determined the relaxation strength  $\Delta \epsilon$  by two different methods: for *i*-PP ( $\beta$ -process) and PS ( $\alpha$ process), the relaxation spectra were fitted with a Havriliak–Negami function (eq 1), while for LDPE  $\Delta \epsilon$ 



**Figure 6.** Relaxation strength  $\Delta \epsilon$  of the dielectric glass transition process vs probe concentration for LDPE (T = 70 °C), PS (T = 135 °C), and *i*-PP (T = 40 °C). The solid lines for LDPE and PS correspond to actual linear fits to the  $\Delta \epsilon$ (c) data points, whereas the dashed line in the case of *i*-PP is just a guide to the eye.

could simply be determined from the increment in  $\epsilon'$ compared to undoped LDPE. The results are summarized in Figure 6, showing a linear relation between the probe concentration and the intensity of the primary relaxation process for LDPE and PS. For *i*-PP, the same trend was found up to a probe concentration of 0.5%; however, the relaxation strength levels off for a DBANS content of 1%. Here one should realize that the actual (local) concentration of probe molecules, which is assumed to be exclusively located in the amorphous phase, is far above the mean probe concentration for the semicrystalline samples. To obtain a more realistic value of the (local) probe concentrations by taking in account the degree of crystallinity (from DSC), one has to correct the mean probe concentrations (used for Figure 6) by a factor of 1.3 and 1.67 in LDPE and *i*-PP, respectively. This means that the only exception from the linear  $\Delta \epsilon$ -(c) behavior that was found for 1% DBANS in *i*-PP refers to the highest local probe concentration ( $q_{ocal} \sim 1.7\%$ ) in all the investigated samples. From fluorescence spectroscopy it is known that at such high probe concentrations aggregation of probe molecules starts to occur, which results in a reduction in the dielectric relaxation strength.

The clear linearity and identical slope observed for LDPE and *i*-PP up to 0.5% probe content also proves that there is no significant fraction of probe molecules entrapped in the crystalline phase, since this would result in the loss of mobile dipoles (below  $T_m$ ) and an thus in a corresponding decrease in relaxation strength, which is not observed.

For PS, a specific offset in the  $\Delta \epsilon(c)$  dependence is visible, the value of which exactly corresponds to the dielectric relaxation strength of the intrinsic  $\alpha$ -process of PS. Nonetheless, the effect of probe addition to PS is linear, implying that the intrinsic dielectric activity and the induced polarity resulting from the probe are additive.

*Relaxation Time of the Primary Relaxation.* So far we have emphasized two essential features of DBANS that qualify this compound as a useful dielectric probe: first, the intensity of the dielectric response associated with the probe molecule scales linearly with the probe concentration, and second, the DBANS probe "amplifies" specifically the dynamic dielectric glass transition process. In the following we want to answer a third crucial question: How accurate does the probe dynamics sense



**Figure 7.** Arrhenius representation of the primary relaxation time for undoped and DBANS-doped PS, *i*-PP, and LDPE samples. All data marked by symbols correspond to peak maximum relaxation times  $\tau_m$  which were obtained by HN fits of isothermal spectra using eq 1. In the two cases of undoped *i*-PP and LDPE, this procedure was not possible due to the absence of sufficiently sharp loss peaks in the frequency domain. Here,  $\tau$  data were evaluated either from isochronal loss curves (LDPE) or from  $\epsilon''(f, T)$  using a recently developed three-dimensional fit techniques (*i*-PP).<sup>53</sup>

 Table 2. Glass Transition Temperatures and Relevant

 VFT Parameters Determined by DRS

				•	
	<i>T</i> <sub>v</sub> [K]	$\log(\tau_{\infty})$	E <sub>v</sub> [kJ/ mol]	$T_{\rm g} = T(\tau = 100 \text{ s}) [^{\circ}\text{C}]$	$T_{g}^{*} = T(\tau = 1 \text{ s}) [^{\circ}C]$
LPDE					
0.1%	182.6	$-13.5^{a}$	16.3	-35.6	-27.4
0.5%	170.1	-13.9	19.0	-40.8	-31.8
1.0%	177.2	-13.6	17.3	-38.3	-29.8
<i>i</i> -PP					
0.1%	203.5	-13.4	16.4	-14.0	-5.6
0.5%	211.0	-11.5	12.2	-20.5	-9.4
1.0%	184.4	-14.9	24.1	-14.3	-4.3
PS					
0%	328.9	-12.0	11.0	96.6	103.4
0.1%	325.4	-12.1	11.6	95.0	102.0
0.5%	328.2	-11.4	9.9	93.4	100.2
1.0%	319.9	-11.5	11.2	90.1	97.7

 $^{a}\,\mathrm{Preexponential}$  factor fixed in fit procedure due to limited set of data.

the relaxation time (distribution) of the primary relaxation?

In Figure 7, an Arrhenius representation of the relaxation time data for the primary relaxation of LDPE, PS, and *i*-PP is given. Clearly, all curves obey the VFT law (eq 2),

$$\tau(T) = \tau_{\infty} \exp\left(-\frac{E_{\rm v}}{k(T-T_{\rm v})}\right) \tag{2}$$

which is the typical signature of the dynamic glass transition. At first glance, there are only minor differences in the relaxation times as a function of the probe concentration as already suggested on the basis of Figures 3–5. For a better quantitative comparison of the relaxation dynamics as a function of the probe content, we have fitted all  $\tau(T)$  data by the VFT equation (eq 2), yielding the three VFT parameters  $T_v$ ,  $E_v$ , and  $\tau_{\infty}$ , which are listed in Table 2. From these parameters, an operationally defined "dielectric"  $T_g$  was then calculated assuming  $\tau(T_g) = 100$  s as a rule of thumb. To compare the dielectric  $T_g$ 's with those obtained from the DMA experiments (measured at f = 1 Hz), an alternative " $T_g$ \*" defined by  $\tau(T_g^*) = 1$  s was computed.

Inspecting the data for LDPE and *i*-PP in Table 2, no clear trend can be seen in the concentration dependence

of both the VFT parameters and the derived dielectric glass transition temperatures. It should be emphasized that all VFT parameters represent unconstrained fit results (with one exception, see footnote Table 2), a fact that is believed to be the main reason for the scatter in the extrapolated  $T_{\rm g}$  values of  $\Delta T_{\rm g} \sim 2.5$  K (LDPE) and  $\Delta T_{\rm g} \sim 3$  K (*i*-PP). Interestingly, these deviations are still smaller than the systematic upshift in the " $T_{\rm g}$ " values by up to 10 K when choosing  $\tau = 1$  s ( $T_{\rm g}^*$ ) instead of  $\tau = 100$  s, which illustrates the usual dilemma of comparing  $T_{\rm g}$  values from DSC data (corresponding to  $\tau \sim 100-1000$  s) with those from DMA experiments (typically  $\tau = 1$  s). Having this is mind, we can conclude that the "dielectric" glass transition temperatures  $T_{\rm g}^*$  are in good agreement with the DMA values given in Table 1.

In contrast to *i*-PP and LDPE, a systematic lowering in the glass transition temperature was found for PS upon addition of DBANS, as found in the calorimetric (see Table 1) and dielectric  $T_g$  (Table 2). Both are in fair agreement with respect to the absolute  $T_g$  values and the maximum  $T_{\rm g}$  shift of 6 K. This finding clearly indicates a significant plasticizing effect of the DBANS molecule on the glass transition dynamics of PS, most likely caused by a "mismatch" in local mobility between the PS backbone and the aliphatic part of DBANS. Here we should recall that the aliphatic tail was specifically introduced to "compatibilize" the rigid-rod type nitrostilbene core to improve its solubility in aliphatic polymer matrices. Consequently, if we had to predict an influence of the probe molecules on the glass transition in LDPE and *i*-PP, we would expect an antiplasticizing effect due to the rigid-rod part of DBANS rather than plasticization. However, none of these scenarios are supported by our experimental findings.

Finally we want to focus on the discrepancy in the relaxation times  $\tau_{\beta}$  between undoped and doped LDPE samples visible in Figure 7. This discrepancy on the order of 1 order of magnitude in relaxation time is counterintuitive since it implies that the "mean" relaxation time of probe reorientation is shorter that the dynamics of LDPE segments. However, inspecting the width of the  $\beta$ -process (cf. Figure 3) in the isochronal representation reveals that the  $\beta$ -peak in undoped LDPE is much broader than that in doped LDPE. A likely explanation for both the shift in (peak) relaxation time and the change in peak width is the preference of the dielectric probe molecules to reside in the most mobile fraction of the amorphous phase, i.e., the least constrained part, while the intrinsic  $\beta$ -peak of LDPE reflects the unweighted diversity of the molecular mobility (spatial distribution) of any polar group outside the crystalline phase. In other words, in a heterogeneous system like semicrystalline LDPE, the dielectric probe specifically senses the most mobile subensemble of polymer segments in the noncrystalline phase. More detailed studies regarding the spatial selectivity of dielectric probes are in progress.

**Fluorescence Spectroscopy.** Temperature-dependent fluorescence measurements were performed for PS, *i*-PP, and LDPE samples. For polystyrene containing 0.1% probe, a gradual increase in intensity, roughly 3.5 times, and a 15 nm red shift of the intensity maximum  $\lambda_{max}$  were observed upon cooling from 180 to 40 °C. No notable changes in emission were observed around the glass transition temperature, although detection of  $T_{g}$  by changes in fluorescence intensity of doped polymers has been reported.<sup>48–50</sup> Increasing the probe content



**Figure 8.** Normalized emission of *i*-PP doped with 0.1% DBANS (180  $\rightarrow$  40 °C with 10 K temperature steps).



**Figure 9.** Normalized emission of *i*-PP doped with 0.5% DBANS (180  $\rightarrow$  40 °C with 10K temperature steps).

resulted in a pronounced decrease in fluorescence intensity, indicating a strong decrease in quantum yield  $\Phi_{\rm f}$  and a 13–20 nm red shift of  $\lambda_{\rm max}$ . However, at 0.5% and 1.0% probe content similar red shifts and increases in intensity upon cooling were observed.

In polypropylene samples doped with 0.1% probe no significant changes in fluorescence are observed upon cooling from 180 to -40 °C. The emission spectra, which exhibit the typical structure that is observed in apolar solvents, gradually shift to the red, while the emission intensity increases. No changes in emission are observed around  $T_{\rm m}$  or  $T_{\rm g}$ . A different behavior is encountered for *i*-PP samples at higher probe concentrations. At high temperatures, in the melt, spectra are similar irrespective of the probe concentration. Upon passing the crystallization temperature major changes in the shape of the emission spectra are observed. The red part of the spectrum around 555 nm increases strongly in intensity and shifts to the red upon further cooling.

Figure 8, showing the normalized fluorescence spectra of *i*-PP doped with 0.1% and 0.5% (m/m) DBANS as a function of temperature, illustrates the spectral changes at different temperatures at these probe concentrations. The observed spectral changes are best visualized by plotting the ratio of the emission intensity at 543 and 569 nm as a function of temperature (see Figure 9).<sup>51</sup> For the 0.1% sample, the intensity ratio shows virtually no changes upon passing the crystallization temperature, but for the 0.5% sample a pronounced change in



**Figure 10.** Intensity ratio I543/I569 for *i*-PP at different concentrations of DBANS as a function of temperature.

slope is observed at 130 °C, the temperature at which crystallization starts. For the 1.0% sample, a more pronounced change of slope is observed at a slightly higher temperature. In addition, instead of a continuous red shift, a blue shift in emission is observed upon cooling below 80 °C.

For LDPE doped with DBANS (Figure 10) a behavior similar to that of *i*-PP was observed. Already at 0.1% DBANS content a clear change in the intensity ratio was found at 110 °C, the temperature at which crystallization starts.<sup>52</sup> Increasing the concentration to 0.5% gave a stronger change in slope, and like in the 1.0% *i*-PP sample, a blue shift in emission at low temperatures. For the 1.0% sample, a shift in gradient is observed at 130 °C, and a more pronounced blue shift below the crystallization temperature is observed. It should be noted that the emission intensity for the 1.0% samples, in both *i*-PP and LDPE is very low, and for obtaining reliable results from fluorescence spectroscopy, lower probe concentrations are highly recommended.

Whereas we did not find any indication of the glass transition in our fluorescence measurements, crystallization of *i*-PP and LDPE was clearly detected by a pronounced red shift in the fluorescence of added probe. This red shift is caused by migration of probe molecules from crystallizing regions, resulting in an increase of probe concentration in the amorphous phase during crystallization. The migration of probe molecules from the crystallizing regions was proven by dielectric spectroscopy. The dielectric strength  $\Delta \epsilon$  did not decrease upon crystallization, which proves that all probe molecules are still in a mobile phase, i.e., expelled from the crystalline phase. From this it is obvious that, during crystallization, an increase of the effective DBANS concentration occurs. To mimic this increase, the fluorescence spectra of DBANS in paraffin oil were recorded as a function of temperature and concentration. Paraffin oil can be considered to be a model system with a polarity and a chemical composition similar to that of the investigated polyolefins.

Figure 11 clearly demonstrates that increasing probe concentration results in red shifts of the emission, in this specific case due to a decrease of the emission band at 480 nm and an increase of the emission band at 560 nm. Figure 12 shows that in paraffin oil the probe emission is particularly sensitive to changes in probe concentration between 0.5 and 1.0%. A strong decrease in emission intensity upon increasing [probe] was also observed.

For 0.5% probe in *i*-PP, the simplest description of probe emission during crystallization would assume that



**Figure 11.** Intensity ratio I505/I530 for LDPE at different concentrations of DBANS as a function of temperature.



**Figure 12.** Normalized fluorescence emission of paraffin oil doped with different concentrations of DBANS.

the intensity ratio coincides with the 0.5% cooling curve at high temperatures until the onset of crystallization, at 130-115 °C, depending on the exact cooling rate. During the crystallization, the probe content in the amorphous phase will increase from 0.5% to 0.8%, and as soon as the crystallization is completed, generally at a temperature  $\pm 10$  °C below the onset of crystallization, the intensity ratio will follow the 0.8% cooling curve. Therefore, a set of straight lines with two opposite changes in gradient at the onset and the end of the crystallization is expected for the cooling curve. From the plots shown in Figures 9 and 10 one is might conclude that such a behavior is not encountered. However, real-time measurements performed on *i*-PP samples containing 0.5% probe confirm this predicted behavior, as illustrated in Figure 14.

Figure 14 shows that the crystallization is observed at different temperatures for different cooling rates, as expected. The onset and the end of the crystallization process are clearly visible and show an excellent correspondence with DSC measurements performed on the same samples under identical conditions. From the heating curves the melting point is observed as a change in gradient accompanied by a small bump. Possibly the change in gradient is observed at melting because the 0.8% and 0.5% curves cross each other at the melting point. The significance of the small bump, apparently superimposed upon the change of gradient, is not elucidated yet. It should be noted that the observed qualitative correlation of these real-time measurements with the behavior expected on the basis of the probe emission in paraffin oil is remarkable since probe distribution in the model system is homogeneous, whereas the probe distribution in the polymer will be



**Figure 13.** Intensity ratio I505/I530 for paraffin oil at different concentrations of DBANS as a function of temperature.



**Figure 14.** Real time-intensity ratio R (I578/I605) for *i*-PP doped with 0.5% DBANS as a function of temperature. Spectra recorded with the real-time fluorescence spectrometer are noncalibrated, which explains the different intensity ratio compared to the traditional fluorescence measurements shown in Figure 10.

inhomogeneous and influenced by the rate of crystallization of the polymer, the rate of diffusion of the probe in amorphous polymer, and the dimensions of both the amorphous and the crystalline regions. In addition, the high viscosity of the polymer might influence probe emissions in a manner that is not covered by the model system.

Crystallization of probe molecules at room temperature was observed for paraffin solutions containing more than 0.5% probe. Therefore, phase separation, not necessarily crystallization of probe, is expected to take place in polyolefins at high local probe concentrations at decreased temperatures. The blue shifts observed upon lowering the temperature in *i*-PP and LDPE samples containing 1% probe are interpreted as being indicative of phase separation. At a constant probe concentration, a red shift is anticipated upon lowering the temperature as indicated by Figure 12. Therefore, a blue shift indicates a decrease of the effective probe concentration. This is most likely caused by a removal of (fluorescent) probe molecules from the system due to phase separation or crystallization of the probe.

In a more general description, a blue shift at constant probe content is caused by a less homogeneous probe distribution. If the probe distribution is inhomogeneous, regions with low probe concentration will dominate the fluorescence, since in these regions the probe has higher fluorescence quantum yields. Phase separation and crystallization of the probe are the obvious ways to



**Figure 15.** Optical micrograph at 110°C of a *i*-PP sample showing spherulites together with droplets of phase-separated DBANS (dark spots) located at the spherulite boundaries. The visible area of the micrograph is  $234 \times 176 \ \mu$ m.

achieve an inhomogeneous probe distribution. It should be noted that during crystallization and melting, migration of the probe will, initially, produce a probe distribution that is inhomogeneous.

Optical Microscopy. An inhomogeneous probe distribution was detected by temperature-dependent optical microscopy experiments on *i*-PP samples containing 1% probe. During crystallization, generally starting at 130 °C, large spherulites are formed in a homogeneously yellow background. At the end of the crystallization around 110 °C, as the spherulites cover the entire surface, dark red regions are formed locally. Upon cooling these red regions remain visible, but upon melting of the polymer crystals they disappear. This implies that solubility and rate of diffusion at 170 °C are high enough to restore a probe distribution that appears to be homogeneous. However, by rapidly repeated melting and crystallization the crystallized samples become more inhomogeneous, and eventually probe droplets about  $1-4 \ \mu m$  in diameter are detected (see Figure 15).

Macroscopic phase separation has also been observed for "old" samples stored at room temperatures for at least a week. Once macroscopic phase separation has occurred heating the sample in the melt for a limited period of time will not restore homogeneity, and the fluorescence and dielectric response of such "old" samples seriously deviates from "new" samples, freshly prepared under high shear conditions. It should be mentioned that phase separation in 1% *i*-PP samples has been detected by dielectric spectroscopy as a lower than expected value of  $\Delta \epsilon$  at high probe concentration. Blue shifts in fluorescence, observed upon lowering the temperature of 1% *i*-PP samples, also indicate phase separation of the probe.

### Conclusions

A new experimental approach is described that allows the convenient study of glass transition dynamics, crystallization, and melting of nonpolar polymers by means of dielectric relaxation and fluorescence spectroscopy.

Small concentrations of polar rigid-rod-like chromophores dissolved in the matrix of nonpolar polymers were proven to act as suitable "dielectric probes" for the study of cooperative dynamics. Due to the lack of internal rotational degrees of freedom of the probe molecule, large-scale fluctuations of the polar axis of the rigid-rod-type probes are effectively coupled to the cooperative dynamics of the matrix, i.e., the dynamic glass transition. In contrast, local dynamics and dynamics involving the crystalline phase essentially do not show up in the dielectric probe response.

From a systematic study of the effect of probe concentration on the dielectric relaxation behavior of three different polymers we can conclude the following:

(i) Addition of the dielectric probe DBANS to *i*-PP, LDPE, and PS modifies the relaxation behavior of the polymers by specifically enhancing the strength of the dielectric glass transition process.

(ii) This "strengthening" is proportional to the mean probe concentration up to about 0.5 DBANS content in polyolefins.

(iii) The relaxation time of the probe relaxation coincides well with the mean relaxation time of the "native" polymer within 1 order of magnitude in frequency.

(iv) Glass transition temperatures deduced from the probe relaxation times are in fair agreement with values determined from DSC and DMA measurements and are in line with data reported in the literature. For PS,  $T_{\rm g}$ values of ~95 °C were found, while LDPE and *i*-PP reveal dielectric  $T_g$ 's ( $\tau = 100$  s) that are slightly lower (LDPE: -38 °C; *i*-PP: -16 °C) than corresponding DSC and DMA data.

Fluorescence spectroscopy revealed that both crystallization and melting of LDPE and *i*-PP are clearly detected. The observed changes in probe emission are explained by migration of probe molecules: from the crystallizing regions during the crystallization process or into the melting regions during the melting process. This probe migration, resulting in effective increases and decreases of probe concentration during crystallization and melting, respectively, was proven with dielectric spectroscopy.

Fluorescence measurements on a paraffin oil model system showed a red shift in emission upon increasing the probe concentration, in particular between 0.5% and 1% probe content. The magnitude of this red shift is similar to the shift that was found with real-time fluorescence measurements for crystallizing *i*-PP and LDPE samples containing 0.5% DBANS. This shows that changes in local probe concentration during crystallization is the major contributor to the spectral changes that occur in these crystallizing polyolefins.

Using higher probe concentrations in *i*-PP and LDPE, above 0.5% m/m, leads to dramatic decreases in fluorescence quantum yield, which seriously decrease the reliability and accuracy of the fluorescence measurements. For these samples, upon decreasing the temperature, blue shifts in emission are observed at lower temperatures, and these blue shifts are attributed to probe aggregation caused by phase separation of the probe from the polymer or crystallization of the probe.

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Supporting Information Available: Figures of DSC, and DMA, for LDPE, i-PP, and PS. This material is available free of charge via the Internet at http://pubs.acs.org.

## **References and Notes**

(1) Kremer, F.; Schönhals, A. Broadband Dielectric Spectroscopy, Springer-Verlag: Berlin, 2003.

- (2) Runt, J. P.; Fitzgerald, J. J. Dielectric Spectroscopy of Polymeric Materials: Fundamentals and Applications, Ameri-can Chemical Society: Washington, DC, 1997.
- (3) Bottcher, C. J. F.; Bordewijk, P. Theory of Electric Polariza*tion*; Elsevier Scientific Pub. Co.: New York, 1978; Vol. 2.
- Hill, N. E.; Vaughan, W. E.; Price, A. H.; Davies, M. Dielectric (4)Properties and Molecular Behaviour; Van Nostrand Reinhold: London, 1969.
- Wübbenhorst, M.; de Rooij, A. L.; van Turnhout, J.; Tacx, J.; Mathot, V. *Colloid Polym. Sci.* **2001**, *279*, 525–531. (5)
- McCrum, N. G.; Read, B. E.; Williams, G. Anelastic and Dielectric Effects in Polymeric Solids; Dover Publications: New York, 1991.
- Boersma, A.; van Turnhout, J.; Wübbenhorst, M. Macromolecules 1998, 31, 7453-7460.
- Simon, G. P.; Runt, J. P. In Dielectric Spectroscopy of Polymeric Materials: Fundamentals and Applications, Fitzgerald, J. J., Ed.; American Chemical Society: Washington, DC, 1997; Vol. 1, pp 329-378.
- (9) Wübbenhorst, M.; Folmer, B. J. B.; van Turnhout, J.; Sijbesma, R. P.; Meijer, E. W. *IEEE Trans. Dielectr. Electr.* Insul. 2001, 8, 365-372.
- (10) Ashcraft, C. R.; Boyd, R. H. J. Polym. Sci., Polym. Phys. Ed. **1976**, *14*, 2153–2193.
- Frübing, P.; Blischke, D.; Gerhard-Multhaupt, R.; Khalil, M. (11)S. J. Phys. D: Appl. Phys. 2001, 34, 3051-3057
- (12) Hoffman, J. D.; Williams, G.; Passaglia, E. J. Polym. Sci., Part C 1966, 173-233.
- (13) Boyd, R. H.; Gee, R. H.; Han, J.; Jin, Y. J. Chem. Phys. 1994, *101*, 788–797.
- (14) Vogel, H. Z. Phys. 1921, 22, 645.
- (15) Fulcher, G. S. J. Am. Ceram. Soc. 1925, 8, 339.
- (16) Tammann, G.; Hesse, G. Z. Anorg. Allg. Chem. 1926, 156, 245.
- (17) Livanova, N. M.; Zaikov, G. E. Polym. Degrad. Stab. 1997, 57, 1-5.
- (18) This dipole moment was calculated with the ChemBats3D software package from Cambridge Software using the AM1 method in combination with a closed cell wave function and Mulliken charges.
- (19) Luckhorst, G. R.; Veracini, C. A. The Molecular Dynamics of Liquid Crystals; Kluwer Academic Publishers: Dordrecht, 1994.
- (20) Williams, G.; Hains, P. J. Chem. Phys. Lett. 1971, 10, 585.
- (21) Shears, M. F.; Williams, G. J. Chem. Soc., Faraday Trans. 2 1973, 69, 1050
- (22) Shears, M. F.; Williams, G. J. Chem. Soc., Faraday Trans. 2 **1973**, *69*, 608.
- (23) Davies, M.; Hains, P. J.; Williams, G. J. Chem. Soc., Faraday Trans. 2 1973, 69, 1785.
- Thurau, C. T.; Ediger, M. D. J. Polym. Sci., Part B: Polym. Phys. 2002, 40, 2463-2472. (24)
- (25)Thurau, C. T.; Ediger, M. D. J. Chem. Phys. 2002, 116, 9089-9099
- (26)Thurau, C. T.; Ediger, M. D. J. Chem. Phys. 2003, 118, 1996-2004.
- (27) Hains, P. J.; Williams, G. Polym. Bull. (Berlin) 1975, 16, 725.
- (28) Several other rigid D- $\pi$ -A molecules have successfully been applied as dielectric probes.
- (29) Loutfy, R. O. Macromolecules 1981, 14, 270-275.
- van Ramensdonk, H. J.; Vos, M.; Verhoeven, J. W.; Mohl-mann, G. R.; Tissink, N. A.; Meesen, A. W. *Polymer* **1987**, (30)951 - 956
- (31) Paczkowski, J.; Neckers, D. C. Macromolecules 1992, 25, 548-553.
- (32) Jager, W. F.; Volkers, A. A.; Neckers, D. C. Macromolecules **1995**, *28*, 8153-8158.
- Jager, W. F.; Lungu, A.; Chen, D. Y.; Neckers, D. C. *Macromolecules* **1997**, *30*, 780–791. (33)
- (34) Vatanparast, R.; Li, S. Y.; Hakala, K. Macromolecules 2000, 33, 438-443.
- Jager, W. F.; Norder, B. Macromolecules 2000, 33, 8576-(35)8582
- (36) Peinado, C.; Salvador, E. F.; Catalina, F. Polymer 2001, 42, 2815-2825.
- (37) Jager, W. F.; Sarker, A. M.; Neckers, D. C. Macromolecules **1999**, *32*, 8791–8799.
- (38) Levenberg, K. Q. Appl. Math. 1944, 2, 164.
  (39) Marquardt, D. J. Soc. Indust. Appl. Math. 1963, 11, 431.
- Jager, W. F.; van den Berg, O. In ACS Symposium Series; Belfield, K. D., Crivello, J. V., Eds.; American Chemical (40)Society: Washington, DC, 2003; Vol. 847, pp 426-436.

- (41) Garo, K.; Donald, R.; Alan, B.; Calundann, G. W.; East, A. J. U.S. Patent 4,957,655, Hoechst Celanese, 1990.
- (42) Using a standard Wittig reaction, the cis isomer is formed along with the desired trans isomer.
- (43) Lupo, D.; Ringsdorf, H.; Schuster, A.; Seitz, M. J. Am. Chem. Soc. 1994, 116, 10498–10506.
- (44) The glass transition temperature is very much dependent on frequency, the rate of cooling, and experimental procedures. Where  $T_g$  is written, read "operationally defined  $T_g$ ".
- (45) There is some debate over this interpretation. In some older reports the -120 °C phase transition is interpreted as the glass transition.
- (46) Donth, E. The Glass Transition. Relaxation Dynamics in Liquids and Disordered Materials, Springer: Berlin, 2001; Vol. 48.
- (47) Boyd, R. H.; Liu, F. In *Dielectric Spectroscopy of Polymeric Materials*; Runt, J. P., Fitzgerald, J. J., Eds.; American Chemical Society: Washington, DC, 1997; pp 128–132.

- (48) Loutfy, R. O.; Teegarden, D. M. Macromolecules 1983, 16, 452-456.
- (49) Ellison, C. J.; Torkelson, J. M. J. Polym. Sci., Polym. Phys. Ed. 2002, 40.
- (50) Ellison, C. J.; Kim, S. D.; Hall, D. B. Eur. Phys. J. E 2002, 8, 155–166.
- (51) This intensity ratio was chosen since it visualizes the changes of the red part of the spectrum.
- (52) For LDPE the optimal intensity ratio (I505/I530) was found to be slightly different from the ratio used for i-PP. For i-PP the major changes were in the red part of the spectrum while for LDPE a notable decrease in intensity in the blue part of the spectrum was also found.
- (53) Wübbenhorst, M.; van Turnhout, J. *J. Non-Cryst. Solids* **2002**, *305*, 40–49.

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