tion chromatography analysis. It was originally thought that these low molecular weight products could be explained according to a simple donor-acceptor model.<sup>7</sup> That is, a high concentration of initiator gives rise to many polymer chains and hence low overall molecular weight. With this theory in mind, some experiments were carried out with small zinc bromide concentrations together with the application of very low current densities. However, these conditions produced no significant increase in molecular weight. The reason for these low molecular weight values is not very clear at present. Further experimental work is now in progress to elucidate the mechanism of termination in these systems.

Thermal polymerization was not observed in blank experiments conducted under conditions already described for electroinitiated polymerization. In the blank experiments, no current was passed through solutions containing N-vinylcarbazole, acetone, and ZnBr<sub>2</sub>. No polymer was found even after the samples had been left for several days in a darkened reaction vessel at room temperature.

In a separate experiment, the locus of polymerization was found, by separation of the electrode compartments using a porous clay battery cup, to be the anode. The locus of polymerization being at the anode eliminates the possibility of an anionic mechanism.

Calculations based on the number of Faradays transferred and the corresponding number of polymer molecules formed indicated a very high absolute electrical efficiency. After 70% conversion at a 5:1 VCZ:ZnBr<sub>2</sub> mole ratio, approximately 70 polymer molecules were formed per electron transferred at the electrode. This is an extremely high efficiency compared with other electrochemical polymerizations and is in sharp contrast to the results obtained by free-radical<sup>13</sup> (< one polymer molecule/electron) or anionic electroinitiation<sup>14</sup> (~ three polymer molecules/electron). It is thought that the high efficiency experienced in this system may be char-

(13) B. L. Funt and K. C. Yu, J. Polym. Sci., 62, 359 (1962).

acteristic of donor-acceptor cationic electroinitiated polymerization.

The asymptotic nature of the conversion-time curves is unusual in that all the curves show a high initial rate during the first 55-80% conversion and then decrease sharply. The polymerizations were always incomplete, thus indicating the occurrence of a high degree of termination. The initial reaction rates appear to be directly proportional to the current density, which might be expected if it is assumed that the rate of initiation is dependent on the concentration of electroexcited VCZ-ZnBr<sub>2</sub> complexes.

Our results indicate that water has an effect on both the rate of polymerization and molecular weight of the polymer. In initial experiments, the water content of the acetone was found to be 0.15% (w/w) by Karl Fisher titration. However, in relatively anhydrous systems (<0.005% H<sub>2</sub>O) low molecular weights were again obtained. These data suggest that the polymerization is proceeding through a cationic mechanism in which chain-breaking reactions or transfer reactions are taking place between the growing polymer cation and VCZ monomer. VCZ monomer is the most basic compound present in this system, and at the concentrations (0.333 *M*) used it seems more likely to be involved in cationic transfer reactions than the water or other basic impurities. The molecular weights obtained in this work are lower than but comparable to those found by Breitenbach.<sup>1</sup>

It seems unlikely that the acetone solvent plays any direct role in determining the molecular weight of the final polymer.

The kinetics and precise mechanism of the reaction will be the subject of further papers involving both electrochemical and photochemical initiation.

Acknowledgment. The authors wish to acknowledge the assistance of Dr. F. Dollish, Mellon Institute, Pittsburgh, Pa., in the nmr analysis.

(14) B. L. Funt and F. D. Williams, J. Polym. Sci., Part A-1, 2, 865 (1964).

# Viscoelastic Properties of Poly(phenylene ethers). II. 2-Methyl-6-alkyl-Substituted Polymers

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ABSTRACT: The viscoelastic properties of a series of 2-methyl-6-(secondary alkyl) poly(*p*-phenylene ethers) have been investigated by dynamic mechanical techniques. No tan  $\delta$  peak was found which could be ascribed to motions of the backbone phenylene unit below  $T_g$ , in agreement with previous work on unsymmetrically disubstituted poly(phenylene ethers). For all the materials studied here two tan  $\delta$  peaks were found between  $T_g$  and  $-200^\circ$ , identified here as the  $\gamma$  and  $\delta$  peaks to conform to previously used nomenclature. The peak temperatures of the  $\gamma$  relaxation increase drastically with the number of CH<sub>2</sub> groups in the side chain (from *ca*. 100 for the C<sub>5</sub> side chain to -50 for C<sub>10</sub> at 1 Hz); the activation energies increase linearly from *ca*. 9 to 18 kcal for these materials. This relaxation is assigned to a low-amplitude hindered torsional oscillation of n - 2units of the alkyl side chain, in its all-trans conformation, around an axis which is coincident with the long axis of the all-trans alkyl chain. The peak temperatures of the  $\delta$  relaxations increase only slightly with increasing side-chain length, the activation energies are uniformly of the order of 6 kcal, and the mechanism seems to be motion of terminal groups (methyl) or ethyl).

The poly(phenylene ethers) constitute a series of polymers that can be modified easily by the placement of various substituents in the 2 and 6 positions of the phenylene ring. A large number of investigations on the viscoelastic properties of this important family of materials have already been made. In a previous paper we have reported on a study of the lowtemperature relaxations encountered in unsubstituted and methyl- or phenyl-substituted  $poly(p-phenylene ethers)^1$  and also reviewed the pertinent literature.

One of the findings of the previous investigation which is

(1) A. Eisenberg and B. Cayrol, J. Polym. Sci., Part C, No. 35, 129 (1971).

relevant to the present study indicated that in unsymmetrically, i.e., 2-methyl-6-phenyl-substituted poly(p-phenylene ether) the relaxation due to hindered torsional oscillation of the main-chain phenylene group ( $\beta$  relaxation, according to the nomenclature of that paper) was absent. Thus, a study of a series of unsymmetrically substituted PPO's should allow us to explore the generality of this phenomenon; furthermore, since part of one of the substituents of the materials studied here contains a linear alkyl chain, it presents the opportunity of investigating alkyl side-chain mobilities as a function of the chain length and comparing the results with those of other alkyl-containing polymers. It was of special interest to see whether the motions of the side chains were associated with those of the backbone, a phenomenon which is encountered in all the other polymers containing alkyl side chains studied to date, or whether the alkyl motions are uncoupled with those of the backbone and thus depend primarily on the chain length.

The materials studied in the present investigation were a series of 2-methyl-6-(secondary alkyl) poly(p-phenylene ethers) made in this laboratory. The monomer has the general structure shown in Figure 1. This general nomenclature of  $MC_n PPO$  will be adopted to describe these materials (where M denotes the methyl in the 2 position and  $C_n$  the alkyl side chain in the 6 position, with n being the total number of carbon atoms in this side chain).

Although owing to the novel aspects of one of the relaxation mechanisms proposed here, it might be useful to review previous work on polymers containing sequences of methylene groups, space limitations, along with the multiplicity of experimental data, make this impossible. Therefore, for the convenience of the reader, only a very brief listing of the most important references will be presented.

Among the studies of short-chain materials should be listed the work of Illers<sup>2</sup> on alkanes, as well as that of Meakins<sup>3</sup> and Dryden<sup>4</sup> on ethers and on solid solutions of ketones and ethers in hydrocarbons. Studies of  $poly(\alpha$ -olefins), which were performed by several groups,<sup>5-8</sup> are also relevant to the present work, as are investigations of other polymers containing alkyl side chains, i.e., the polymethacrylates7,9-16 and the poly(vinyl alkyl ethers);<sup>17</sup> these were reviewed extensively by McCrum, Read, and Williams.<sup>18</sup> The series of poly-(chloroalkyl methacrylates) studied by Mikhailov, et al., 19

(2) K.-H. Von Illers, Rheol. Acta, 3, 185 (1964).

(3) R. J. Meakins, Progr. Dielectrics, 3, 153 (1961); Trans. Faraday Soc., 55, 1694 (1959), and references herein

(4) J. S. Dryden and S. Dasgupta, ibid., 51, 1661 (1955); J. S. Dryden and H. K. Welsh, ibid., 60, 2135 (1964).

(5) K. J. Clark, A. T. Jones, and D. J. H. Sandiford, Chem. Ind. (London), 2, 2010 (1962).

(6) M. Takayanagi, Pure Appl. Chem., 23, 2, 151 (1970).
(7) A. H. Willbourn, Trans. Faraday Soc., 54, 717 (1958)

- (8) T. F. Schatzki, Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem., 6, 646 (1965).
  - L. De Brouckere and G. Offergeld, J. Polym. Sci., 30, 105 (1958).
- (10) H. Sasabe and S. Saito, J. Polym. Sci., Part A-2, 6, 1401 (1968).
   (11) J. D. Ferry and S. Strella, J. Colloid Interface Sci., 13, 459 (1958).
- (12) G. P. Mikhailov and T. I. Borisova, Sov. Phys. Tech. Phys., 3,
- 120 (1958); G. P. Mikhailov, J. Polym. Sci., 30, 605 (1958)
- (13) W. P. Slichter and E. R. Mandell, J. Appl. Phys., 30, 1473 (1959).
   (14) E. A. W. Hoff, D. W. Robinson, and A. H. Willbourn, J. Polym. Sci., 18, 161 (1955).

(15) J. G. Powles, B. I. Hunt, and D. J. H. Sandiford, Polymer, 5, 505 (1964).

(16) R. A. Haldon and R. Simha, Macromolecules, 1, 340 (1968); J. Appl. Phys., 39, 1890 (1968).

(17) R. A. Haldon, W. J. Schell, and R. Simha, J. Macromol. Sci. B, 1, 759 (1967); W. J. Schell, R. Simha, and J. J. Alkonis, J. Macromol. Sci. A, 3, 1297 (1969).
(18) N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids," Wiley, New York, N. Y., 1967.
(10) C. P. Mitheilaw and T. Bacima, Macromol. New York, N. Y., 1967.

(19) G. P. Mikhailov and T. I. Borisova, Vysokomol. Soedin., 6, 1778 (1964).



Figure 1. Structure of the monomer in MC<sub>2</sub>PPO's (where 5 < n < 110).

should also be mentioned. Several polymer series with methylene sequences in the backbone have also been investigated. Among these should be mentioned the work of MacKnight, et al., 20 on polyurethanes, and that of Sinnott 21 on polyethylene.

A thorough review of the above literature reveals that in studies of molecular motions of noncrystalline polymers containing alkyl side chains or methylene sequences, there are no examples of  $\beta$  or  $\gamma$  relaxations that do not parallel the main  $\alpha$  relaxation in its temperature behavior, possibly implying some type of coupling, at least between  $T_{\beta}$  and the  $\beta$  relaxation. The activation energies corresponding to the sub- $T_g$ motions of these groups do not present us with a general trend that resembles that found in the long-chain crystalline compounds, in which an increase in the activation energy or peak temperature generally accompanies an increase in the chain length. The polyurethanes in which CH<sub>2</sub> groups are present in the backbone between various other groups are the only series which shows an irregular but general increase in the activation energies with the lengthening of the methylene sequence. Apart from this case, an increase in the length of the amorphous alkyl side chain is not accompanied by a regular increase in the activation energy related to the motions of this side chain in polymeric materials. Since, as it turns out, the motion of the alkyl side chain in our materials is not coupled to the primary glass transition, the series of MC<sub>n</sub>PPO in which secondary alkyls are attached to phenylene units constituting the backbone seem very well suited to a study of sub- $T_{g}$  motions and their temperature dependence independent of the main glass transition.

#### (I) Experimental Section

(A) Synthesis of Monomers. The monomers used in this work were prepared by an adaptation of the method originally described by Ecke.22 All monomers were prepared from highpurity o-cresol by alkylation with an olefin in the presence of aluminum cresolate catalyst.

A typical preparation was as follows. An autoclave was charged with aluminum turnings (1.0 g) and o-cresol (50 g) under nitrogen. The reaction mixture was slowly heated with agitation to 240° and then allowed to cool to room temperature. The autoclave was vented to remove hydrogen, then 1-octene (15 g) was injected. The mixture was heated to 150°, held at this temperature for 90 min and cooled once more to room temperature.

The reaction product was shaken with a mixture of toluene, water, and concentrated HCl (50 ml, 4:4:1) and the organic layer was separated, washed several times with water, dried, and distilled. The distillation yielded unreacted octene (3.0 g) and an alkylated phenol fraction (114-152° at 14 Torr; 20.0 g). The alkylphenol was purified by chromatography on Fisher 950 silica gel, eluting with a benzene-petroleum ether (30-60°) equal-volume solvent. From the leading fractions 2-methyl-6(1-methylheptyl)phenol (18 g) was isolated by distillation (150-52° at 15 Torr).

(22) G. G. Ecke and A. J. Kolka, U. S. Patent 3,075,832 (1963).

<sup>(20)</sup> T. Kajiyama and W. J. MacKnight, Macromolecules, 2, 254 (1969).

<sup>(21)</sup> K. M. Sinnott, J. Appl. Phys., 37, 3385 (1966).

TABLE I PREPARATION CONDITIONS AND PROPERTIES OF MONOMERS <sup>4</sup>						
Mon- omer	Olefin/ cresol	Reaction temp, °C	Crude yield, % <sup>b</sup>	Bp, °C (P, Torr)	Rj <sup>c</sup>	
C1					0.26	
$C_5$	5	128	55	126 (19)	0.50	
$C_6$	6	128	60	136 (20)	0.50	
$C_7$	6	150	80	146 (16)	0.53	
$C_8$	4	150	80	155 (16)	0.50	
$C_{10}$	5	150	80	192 (17)	0.61	
C14	5	165	77	236 (21)	0.64	
$C_{16}$	4	170	75	176 (1)	0.74	
$C_{20}$	5	170	70	242 (1)	0.71	

<sup>a</sup> All reactions run for 90 min after achievement of reaction temperature. <sup>b</sup> Yield before column chromatography. <sup>c</sup>  $R_f$  values determined by thin layer chromatography of purified products on silica at 23° with benzene-petroleum ether (1:1 v/v) eluent.

The optimum conditions for preparation of each monomer were slightly different, and details are presented in Table I. The final products were characterized by infrared and nmr spectroscopy, thin layer chromatography, and elemental analysis. No impurities were detectable by any of these techniques, and the upper limit for 2-methyl-4-alkylphenol impurities was estimated by infrared spectroscopy to be less than 1%.

(B) Synthesis of Polymers. The polymers were synthesized using copper complex catalyzed oxidative coupling.23 The major problems encountered were the achievement of sufficiently high molecular weight to prepare samples for dynamic mechanical measurements and to optimize yields of polymer. Many variations of catalyst, solvent, and reaction conditions were tried. The best system proved to be a modification of that described by Yudkin, et al.<sup>24</sup> The standard polymerization screening procedure was as follows.

A stream of oxygen (600 ml/min) was passed through a mixture of dimethylformamide (DMF) (15 ml), xylene (15 ml), and pyridine (10 ml) containing a suspension of freshly prepared cuprous chloride (0.2 g). After 20 min at the required polymerization temperature (25°), a sample of monomer (2.0 ml) was injected and polymerization was continued for 90 min. The reaction mixture was then added to excess methanol containing concentrated HCl (5% v/v) to precipitate the polymer. After filtration, the polymer was redissolved in toluene and precipitated in pure methanol several times before drying under vacuum.

Polymers were characterized by infrared and nmr spectroscopy.

Large samples of polymer were prepared by proportional scale up of the above procedure.

(C) Sample Preparation. For both torsional pendulum and vibrating reed measurements, samples of the usual dimensions were prepared by compression molding at  $T_g + 10-50^\circ$  under 3000 psi for 5-10 min. Prior to molding, the samples were degassed for 3 days under vacuum (0.1 mm) at about their respective glasstransition temperatures. After molding, all the samples, transparent and yellowish in color, were kept under vacuum to reduce moisture uptake. The films for all the MC<sub>n</sub>PPO series up to MC<sub>8</sub>PPO were tough, while above that point, rubbery or liquid behavior was encountered.

(D) Measurements. Dynamic mechanical measurements on MC<sub>5</sub>PPO up to MC<sub>10</sub>PPO were carried out over a frequency range of 0.2-4 cps and from  $-200^{\circ}$  to  $T_{g}$  with a torsional pendulum, and from 30 to 1000 cps between  $-140^{\circ}$  and room temperature with a vibrating-reed apparatus.25



Figure 2. Tan  $\delta$  behavior of MC<sub>6</sub>PPO at various frequencies: (O)  $0.5, (\bullet) 3, (\Delta) 45, (\Box) 75, (\bigcirc) 665 \text{ cps.}$ 

#### (II) Results

(A) Preparation and Properties of Monomers. The reaction of a 1-olefin with o-cresol in the presence of an aluminum cresolate catalyst, under optimum experimental conditions, yields the 2-methyl-6-(secondary alkyl)phenol in very high yield. The small amounts of 2-methyl-4-alkylphenol produced are readily removed by column chromatography on silica, since the latter have much higher retention times than the highly sterically hindered 2,6 derivatives. Within the limits of detectability by nmr spectroscopy, the alkylations resulted exclusively in the 1-methylalkyl products.

The infrared spectra of the monomers showed all of the bands expected for a 2,6-dialkylphenol. In particular, the following features were noted: (a) two bands in the 730-740and 760-770-cm<sup>-1</sup> region characteristic of ortho substitution; (b) no band in the 800-820-cm<sup>-1</sup> region characteristic of para substitution: (c) three bands at 1775, 1835, and 1895  $cm^{-1}$ characteristic of ortho substitution; (d) a band at 710-715 cm<sup>-1</sup>, increasing in intensity with increasing length of the alkyl side chain. This band may be assigned to the aliphatic methylene "rotation" mode expected in this region.

The nmr spectra of the monomers confirmed their structure as the one shown in Figure 1. The positions of the resonances  $(\delta, ppm)$  were as follows: (a) 6.6-7.1, (b) 4.50, (c) 3.00, (d) 2.20, (e) 1.51, (f) 1.25, (g) 0.88, (h) 1.18. The complete absence of a sharp singlet at 1.33 ppm was diagnostic of the absence of gem-dimethyl substitution at the  $\alpha$ -carbon and indicated that side-chain isomerization impurities were absent. The general sharpness of the nmr spectra was also indicative of the absence of significant isomeric impurities.

(B) Preparation and Properties of Polymers. Under the conditions used in the present study, solid polymers of reasonable mechanical strength were obtained from monomers with

<sup>(23)</sup> A. S. Hay, Advan. Polym. Sci., 4, 496 (1967).
(24) B. I. Yudkin, K. N. Oleinikova, and V. N. Odinokov, Sov. Plastics, 8, 29 (1968).

<sup>(25)</sup> S. Reich and A. Eisenberg, Rev. Sci. Instrum., 41, 1904 (1970).

TABLE II
SUMMARY OF THE RELAXATION MECHANISMS OF THE $POLy(p$ -phenylene ethers)

Com- pound	T <sub>g</sub> , °C	$T_{\beta}$ , °C (1 Hz)	$E_{\beta}$ , kcal	$T_{\gamma}$ , °C (1 Hz)	$E_{\gamma}$ , kcal	$T_{\delta}$ , °C (1 Hz)	$E_{\delta}$ , kcal
H₂PPO	$\sim 80^a$	-113 <sup>b</sup>	$13 \pm 2$				
H <sub>2</sub> PPS		$-108^{b}$	$11 \pm 2$				
M <sub>2</sub> PPO	205	- 55 <sup>b</sup>	$16 \pm 3$				
MPhPPO	180	g		$\sim -135^{\circ}$	$12 \pm 2$	Not measurable <sup>d</sup>	
Ph <sub>2</sub> PPO	220	+80%	$23 \pm 3$	-135°	$12 \pm 2$	-190 <sup>d</sup>	$4 \pm 2$
MC <sub>5</sub> PPO	100	g		-102	$9\pm0.5$	-192 <sup>f</sup>	6 ± 2
MC <sub>6</sub> PPO	85	g		-90e	$10 \pm 1$	-1851	$7\pm2$
MC <sub>7</sub> PPO	60	g		- 78°	$12 \pm 1$	-178	$6 \pm 2$
MC <sub>8</sub> PPO	54	g		-67°	$14 \pm 1$	180/	$6 \pm 2$
MC <sub>10</sub> PPO	20	g		49°	$18 \pm 1$	-179 <sup>7</sup>	$7 \pm 2$
MC <sub>14</sub> PPO	$\sim -10$	g		h		Not meas	sured

<sup>e</sup> From literature. <sup>b</sup> Hindered torsional oscillation of backbone phenylene units. <sup>e</sup> Hindered torsional oscillation of side-chain phenyl units. <sup>d</sup> Hindered "wagging" of side-chain phenyl units. <sup>e</sup> Low-amplitude hindered torsional oscillation of alkyl side chain in planar zig-zag conformation along the long axis. <sup>f</sup> Hindered rotation of terminal group (methyl or ethyl). <sup>e</sup> Backbone phenyl oscillations not observable in these materials due to asymmetry. <sup>h</sup> At this point  $\gamma$  transition has coalesced with  $T_g$ .

secondary alkyl side chains up to  $C_8$ . Above that limit the polymers were rubbers, or gums. As will be seen below, this factor is due to the low glass-transition temperature of the polymers with side chains  $>C_{10}$ .

The presence of a long-chain alkyl group seems to inhibit polymerization and favor C-C coupling. Even under optimum conditions, 2-methyl-6-*sec*-eicosylphenol only gave a 25% yield of polymer.

(C) Dynamic Mechanical Studies. A series of tan  $\delta$  runs for MC<sub>6</sub>PPO from 0.45 to 665 cps and -200 to  $+20^{\circ}$  is shown in Figure 2. No additional relaxations between  $20^{\circ}$  and  $T_g$  (+80°) were found. All samples showed a similar behavior as a function of temperature in that they exhibited only two relaxations between  $T_g$  and  $-200^{\circ}$ . These two relaxations, in order of decreasing temperature, are labeled  $\gamma$  and  $\delta$ ; for reasons mentioned below, the symbol  $\beta$  is not used here. The locations of these peaks were dependent upon the length of the side chain and naturally upon the frequency of measurement, and activation energies were obtained for the sub- $T_g$  processes.

The dynamic mechanical results are summarized in Table II. For the sake of completeness, the relevant results of the previous study on unsubstituted or rigidly substituted PPO's are also included. To keep a consistent nomenclature, the letter  $\beta$  is assigned to hindered torsional oscillation of mainchain phenylene units;  $\gamma$  is reserved for hindered torsional oscillation of the side chain as a whole (phenyl group) or of a major portion thereof (linear segment of alkane in planar zig-zag conformation), while the letter  $\delta$  is assigned to either hindered wagging of side-chain phenyl groups or rotation of terminal groups on the alkyl side chain. As will be shown below, the  $\beta$  relaxation does not occur in the MC<sub>n</sub>PPO series. The mechanistic assignments given in Table II will be justified in sections III and IV.

The location in temperature of the  $\gamma$  and  $\delta$  peaks are seen in Figure 3 for a frequency of *ca.* 3 cps. It is evident from Table II and Figure 3 that the position of the  $\gamma$  peak at constant frequency in the MC<sub>n</sub>PPO family goes up with the number of CH<sub>2</sub> groups and that the activation energies also increase with the increased length of the side chain. Figure 4 summarizes the activation energies of the five polymers by presenting their frequency *vs.* 1/*T* behavior. While the glasstransition peak goes down in temperature when *n* increases,



Figure 3. Tan  $\delta$  behavior of MC<sub>n</sub>PPO's at *ca*. 3 cps.

the  $\gamma$  peak moves up; in MC<sub>14</sub>PPO they have coalesced into one single broad relaxation.

The location of the  $\delta$  relaxation lies near the low-temperature limit of our instrument; thus the activation energies determined are of relatively low precision. An increase in the side-chain length results in an increasing  $\delta$  relaxation temperature for the shorter alkyl groups, but in the MC<sub>7</sub>-, MC<sub>8</sub>-, and MC<sub>10</sub>PPO this relaxation is present at about the same temperature. The activation energies, also summarized in Table II, are constant for all the five compounds within experimental error.

The heights of the  $\gamma$  and  $\delta$  relaxations are sensitive to the



Figure 4. Loc i of the  $\gamma$  relaxations: (O) MC<sub>5</sub>PPO, ( $\bullet$ ) MC<sub>6</sub>PPO, ( $\Delta$ ) MC<sub>7</sub>PPO, ( $\Box$ ) MC<sub>8</sub>PPO, ( $\bigcirc$ ) MC<sub>10</sub>PPO.



Figure 5. Variation of the activation energies of the  $\gamma$  relaxation in MC<sub>n</sub>PPO's with side-chain length.

length of the side chain of each  $MC_nPPO$ ; for both processes the tan  $\delta$  maxima increase with an increase of *n*.

### (III) Theoretical Section

A plot of the activation energies of the  $\gamma$  relaxation of the five MC<sub>n</sub>PPO's vs. the side-chain length yields a straight line (Figure 5). For reasons that will become apparent later, the activation energies are plotted against n - 2 rather than n. Since this behavior is very similar to the one encountered in the crystalline long-chain ethers and esters in which the entire chain is known to move within the crystal, it is tempting to ascribe the  $\gamma$  relaxation in our system also to motions of the alkyl side chains, in a manner analogous to that which is observed in these crystalline materials. Further evidence supporting this assignment can be summarized as follows.

In the previous paper it was shown that the relaxation due to hindered torsional oscillation of the phenylene groups for  $M_2PPO$  occurred at  $ca. -50^\circ$  for 1 cps and that an increase in the moment of inertia of the backbone raised the temperature of the tan  $\delta$  maximum (up to  $+80^\circ$  for Ph<sub>2</sub>PPO). The main sub- $T_g$  relaxation for the MC<sub>5</sub>PPO, which is the material with the lowest moment of inertia studied here, occurs at ca. $-100^\circ$ , which is well below the temperature which would be expected from our experience with other PPO's if it were due to backbone phenylene oscillations. For the  $\beta$  relaxation, the peak positions and activation energies of the unsubstituted or rigidly substituted PPO's described in the previous paper could be correlated within the framework of the O'Reilly and Tsang formalism. An attempt to do so for the polymers studied here, assuming the same type of mechanism, was unsuccessful, with experimental and theoretical results diverging drastically.

By contrast, the theoretical arguments which are based on the assumption that the  $\gamma$  relaxation of these materials is due to oscillations of the alkyl chain in its planar zig-zag form yields excellent correlation between theory and experiment. The theory used here is based on that of Hoffman, Williams, and Passaglia<sup>26</sup> and is described more fully below.

Parallel studies were made on short-chain alkanes embedded in different polymeric matrices (polystyrene, PIB, polypropylene). The results of these studies, which will be part of a forthcoming publication, showed a regular increase in the activation energy with the increase in length of the alkane in a fashion similar to the one observed in the  $MC_nPPO$ 's.

The details of the application of the theory of Hoffman, Williams, and Passaglia to our materials will now be presented to explain the behavior of the  $\gamma$  relaxation in the MC<sub>n</sub>PPO series. We stress, however, two main differences from their original model. (1) There is no crystalline character in this series of polymers. (2) Since the side chain is attached to the backbone the only motion that it can be subject to is one of rotation without longitudinal translation.

Our model therefore envisages a hindered torsional oscillation of the planar zig-zag with a pivot point between carbon atoms c and e (see Figure 1), with a slight motion of the methyl group attached to carbon c, and very low amplitude motions between carbon atom c and the ring. Using any of the space-filling models, it is easy to show that this type of motion is indeed possible. In their hindered torsional oscillations around the long axis of the linear alkyl chain, all the CH<sub>2</sub> groups of this chain in its zig-zag configuration go from one site A to another site B, the energy barrier being the same for motion in either direction. However, upon application of a mechanical deformation the barrier changes to  $\Delta Q + E$ for going from A to B and  $\Delta Q$  for going from B to A. Following the usual formalism, the transition probabilities for hopping from A to B and back can be written as

$$W_{AB} = A'e^{-(\Delta Q + E/kT)}$$
$$W_{BA} = A'e^{-\Delta Q/kt}$$

with<sup>27</sup>

or

$$A' = \frac{N}{2\pi} \left(\frac{2kT}{\pi I}\right)^{1/2} \tag{1}$$

(2)

N is a number related to the number of minima in the barrier per  $360^{\circ}$ , and, for most hindered rotations, ranges from 1 to 6; I is the moment of inertia of the rotating CH<sub>2</sub> groups of each compound. The relaxation time is

 $\tau = \frac{1}{2(W_{AB} + W_{BA})}$  $\tau \cong \frac{1}{B} e^{\Delta Q/kT}$ 

(26) J. D. Hoffman, G. Williams, and E. Passaglia, J. Polym. Sci., Part C, No. 14, 173 (1966).

(27) D. E. O'Reilly and T. Tsang, J. Chem. Phys., 46, 1300 (1967).

with B = 2A'. But

$$\Delta Q = \Delta H - T \Delta S \tag{3}$$

Further, the enthalpy and entropy are broken down into

$$\Delta H = \Delta H_{1-2} + p \Delta H_{\rm CH_2}$$

and

$$\Delta S = \Delta S_{1-2} + p \Delta S_{\rm CH_2}$$

with p = n - 2, since this is the number of moving CH<sub>2</sub> groups.  $\Delta H_{1-2}$  and  $\Delta S_{1-2}$  refer to the activation enthalpy and entropy associated with the motion of carbon atom c and the pendant methyl group (Figure 1), while the subscript  $CH_2$ refers to the same quantities of the CH<sub>2</sub> or CH<sub>3</sub> units along the linear chain segment made of p units. We substitute these quantities in eq 3 and then insert eq 3 in eq 2. Solving for T (for 1 mol), one obtains

$$T = \frac{\Delta H_{1-2} + p\Delta H_{\rm CH_2}}{R \log B\tau + \Delta S_{1-2} + p\Delta S_{\rm CH_2}}$$
(4)

Replacing T by  $T_{\gamma}$ , the temperature at which the  $\gamma$  relaxation occurs, and  $\tau$  by  $\tau_m$ , the relaxation time corresponding to a frequency of 1 Hz, eq 4 can be rewritten as

.

$$T_{\gamma} = \frac{\Delta H_{\rm CH_2}}{\Delta S_{\rm CH_2}} \left[ \left( \frac{\Delta H_{1-2}}{\Delta H_{\rm CH_2}} \right) + p \right] \times \left[ \frac{\Delta S_{\rm CH_2}}{R \log B\tau_{\rm m} + \Delta S_{1-2} + p \Delta S_{\rm CH_2}} \right]$$

This gives for  $T_{\gamma}$  an equation which is exactly analogous to that of Hoffman, et al., i.e.

$$T_{\gamma} = T_0 \frac{a+b}{b+p} \tag{5}$$

with

$$a = \frac{\Delta H_{1-2}}{\Delta H_{\rm CH_2}} \tag{6}$$

$$T_0 = \frac{\Delta H_{\rm CH_2}}{\Delta S_{\rm CH_2}} \tag{7}$$

$$b = \frac{R \log B\tau_{\rm m} + \Delta S_{1-2}}{\Delta S_{\rm CH_2}}$$
(8)

Following the lead of Hoffman, et al., the enthalpy term is the experimentally determined activation energy; therefore, from the curve of the activation energies of the five compounds vs. n-2 one can obtain the values

$$\Delta H_{\rm CH_2} = 1.8$$
 kcal (slope)

$$\Delta H_{1-2} = 3.6$$
 kcal (intercept)

From this one obtains a = 2.0. When  $\Delta Q$  is replaced by  $\Delta H - T\Delta S$  in eq 2 and a plot is made of log frequency vs. 1/T for all the materials, an extrapolation to  $1/T \rightarrow 0$  gives the successive maximum frequencies from which respective  $\Delta S$  values for each compound are calculated. The increment per CH<sub>2</sub> unit,  $\Delta S_{CH_2}$  is then obtained as  $\Delta S_{CH_2} \simeq 5.3$  eu. This, in turn, when inserted into eq 7, gives

$$T_0 \simeq 340$$

By inserting different experimental values of  $T_{\gamma}$  at 1 cps and the corresponding p's into eq 5, b can be calculated: the result is  $b = 7 \pm 0.5$ . Therefore, the complete equation is

$$T_{\gamma} = 340 \left( \frac{2.0 + p}{7.0 + p} \right)$$
 (5A)

TABLE III						
Compound	р	$T_{\gamma}$ (exptl), °C	$T_{\gamma}$ (calcd), °C			
MC <sub>5</sub> PPO	3	-102	-103			
MC <sub>6</sub> PPO	4	<b>9</b> 0	-88			
MC7PPO	5	78	-75			
MC <sub>8</sub> PPO	6	-67	-64			
MC10PPO	8	- 49	-47			

Equation 5A correlates the position of the  $\gamma$  peaks at 1 cps with the chain length of each  $MC_n PPO$ . Table III shows the correspondence between the calculated and experimental values of  $T_{\gamma}$  recalculated in degrees Celsius for convenience. The relation shown in Table III is of the same type as the one found for alkanes and other long-chain crystalline compounds. Finally, to calculate  $\Delta S_{1-2}$ , we proceed as follows.

From eq 1 and the appropriate values of I, etc., for the different compounds it is possible to calculate A'. Depending upon the value of N, A' varies between ca. 0.3  $\times$  $10^{12}$  for N = 1 to ca.  $2 \times 10^{12}$  for N = 6. Taking the average value of 1012 and inserting it in eq 8, one can obtain for  $\Delta S_{1-2}$  a value of  $\sim -15$  eu.

## (IV) Discussion

The glass-transition temperature of the series of polymers studied here decreases with an increase in the side-chain length in a manner which is analogous to other series of materials. The rate of change of  $T_g$  per number of CH<sub>2</sub> units with the lengthening of the chain is comparable to the one found in the polymethacrylate series. In our series  $dT_g/dn \simeq$ 16, while in the polymethacrylates over the same length of side chain  $dT_g/dn \simeq 12.^{16}$ 

The absence of the  $\beta$  relaxation in the MC<sub>n</sub>PPO's has been discussed in the theory section and will not be repeated here. The generality of this absence in the unsymmetrically disubstituted PPO's is consistent with some type of packing effect as was pointed out in the previous paper.

Perhaps the most important single result of the present study is the finding that in contrast with other series of materials possessing alkyl side chains, the  $\gamma$  relaxation is uncoupled from those motions of the backbone which give rise to the glass transition. This uncoupling can best be seen in the fact that while the  $T_g$  of the polymer decreases as the chain length increases, the  $\gamma$  relaxation exhibits the opposite trend. While these trends do not necessarily prove the absence of coupling, they are a strong indication of it. The question arises as to whether the uncoupling of the  $\gamma$ relaxation from  $T_{\rm g}$  is due to the fact that the  $\beta$  relaxation is absent. This may very well be the case, which in turn suggests the possibility that, in general, if the glass transition represents the temperature of the onset of backbone oscillatory motions, then the side-chain motions which occur at a lower temperature are uncoupled from it. If, however, a  $\beta$  relaxation exists which may be caused by motions of backbone segments as in the polymethacrylates, then the side-chain motions may be coupled to  $T_g$ , and consequently the position of the  $\gamma$  relaxation depends as much on the glass-transition temperature as on the nature of the side chain, if not more. It should be stressed that the  $MC_nPPO$  series is the only family of materials in which such an uncoupling has been observed; much additional work is needed to confirm the generality of the observation.

It might be worthwhile to comment on the magnitude of the value of enthalpy and entropy obtained in section III.

Our value for  $\Delta H_{CH_2}$  is 1.8 kcal. This value is somewhat higher than that obtained by Meakins<sup>3</sup> for long-chain ethers, esters, and solid solutions of ketones (700 cal/CH<sub>2</sub>) [or by Broadhurst<sup>28</sup> for the enthalpy of fusion of long-chain paraffins (~1 kcal/CH<sub>2</sub>)]. It is important to remember, however, that those materials are crystalline and that therefore a displacement of the chain as a whole along the C axis is also present. In our case the higher value of  $\Delta H_{CH_2}$  of 1.8 kcal is not surprising, in view of the fact that we are dealing with a noncrystalline environment and also that longitudinal displacement is impossible. Hoffman, et al., 26 in their attempt to calculate  $\Delta S_{CH_2}$ , theoretically obtained values of 2 to 3 eu, values which correspond to those found experimentally for long-chain paraffins by Broadhurst. Our value of 5.3 eu is in line with those of the above studies. The similarity of  $\Delta S_{CH_2}$ as well as the closeness of the  $\Delta H_{\rm CH_2}$  values lend further support to our mechanistic assignment for the  $\gamma$  relaxation.  $\Delta H_{1-2}$  and  $\Delta S_{1-2}$  in our series have, of course, a completely different origin than those encountered in the other materials, so no meaningful comparison is possible.

The negative value of  $\Delta S_{1-2}$  (-15 eu) cannot be taken as very significant in itself. It is the total entropy related to the motion of the pivot point *and* to the motion of the linear alkyl portion of the side chain that should be considered.

(28) M. G. Broadhurst, J. Chem. Phys., 36, 2578 (1962).

In the case of MC<sub>5</sub>PPO, which possesses the smallest side chain, this total entropy  $[\Delta S_{1-2} + 3(\Delta S_{CH_2})]$  is of the order of 0–1 eu, and the corresponding activation energy is 9 kcal/mol. Similar cases in which processes having small activation energies and very small entropies (or even negative entropies) have been reported previously. For example, the dielectric relaxation of dioctyl phtalate in polystyrene found by Levi<sup>29</sup> had an activation energy of 5 kcal/mol and an entropy of -2 eu. For higher activation energy processes, Levi observed a positive and higher value of the entropy, as is the case with the MC<sub>n</sub>PPO's when the side chain of the secondary alkyl increases in length.

Finally, it should be pointed out that while our assignment of the  $\delta$  mechanism is speculative, we are confident that its origin lies in the alkyl chain. This is confirmed by the fact that a peak of comparable intensity and position in temperature is encountered by Illers in his study of alkanes embedded in polystyrene. Since in those materials, this peak cannot arise from a motion outside the chain, we believe that this is true in our system also; furthermore, the identity of the activation energies suggests that we are dealing with the same group in our entire series.

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(29) D. L. Levi, Trans. Faraday Soc., 42, 152 (1946).

# Dependence of Butadiene Polymerization Rate on Monomer Concentration for Some *π*-Crotylnickel Iodide Catalysis

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**ABSTRACT:** An extensive study of the effect of monomer concentration for the title reaction indicates that the previously reported first-order dependence on monomer is only true for low monomer concentrations. The order is 0.5 at the highest experimental monomer concentration, but data indicate that it extrapolates to <0.5 at still higher monomer concentration. Since the nonideality of the butadiene-benzene system is known to be too small to account for this behavior, a kinetic origin is proposed. A mechanism involving precoordination of two monomer molecules to the inactive catalyst dimer is proposed.

In a previous report we described results of a kinetic study of the polymerization of butadiene by  $\pi$ -crotylnickel iodide (1).<sup>1</sup> At that time it was concluded that the rate exhibited a strict first-order dependence on monomer concentration in the range 0.3-3.0 *M* butadiene. A similar conclusion had been previously arrived at by Lazutkin, *et al.*, using a  $\pi$ -allylnickel iodide catalyst.<sup>2</sup> Subsequent to our original measurements, we have made several new and more detailed series of measurements, both on the pure  $\pi$ -crotylnickel iodide catalyst and on this catalyst partially deactivated by reaction with benzoyl peroxide.<sup>3</sup> These measurements have shown that there is a substantial departure from first order monomer dependence at high monomer concentrations.

#### Results

The influence of monomer concentration on the reduced rate for a variety of catalyst concentrations in benzene is shown in Figure 1. The reduced rate is defined as the observed rate in moles per liter per second divided by the square root of the catalyst concentration, and eliminates the influence of the latter (see ref 1). In addition to pure catalyst runs, a pair of duplicate runs using equimolar catalyst and benzoyl peroxide is also included. In the latter case the reduced rate was calculated assuming that benzoyl peroxide destroys catalyst dimer on a two to one molar basis.<sup>8</sup>

The data in Figure 1 give a slope at lower monomer concentrations that is close to unity. However, it is clear, from both visual inspection and from the computer plotted best line, that the slope diminishes at high monomer concentration. This effect is much more evident in Figure 2, which shows the variation of slope (reaction order) of the line in

<sup>(1)</sup> J. F. Harrod and L. R. Wallace, Macromolecules, 2, 449 (1969).

<sup>(2)</sup> A. M. Lazutkin, V. A. Vaskevitch, S. S. Medvedev, and V. N. Vasileva, Dokl. Akad. Nauk SSSR, 175, 859 (1967).

<sup>(3)</sup> L. R. Wallace and J. F. Harrod, Macromolecules, 4, 656 (1971).