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Thermally reversible crosslinked polyethylene using Diels–Alder reaction in molten state

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ABSTRACT

Thermally reversible crosslinked polyethylene was prepared by Diels–Alder (DA) and retro Diels–Alder (rDA) reaction. Maleimide/furan adduct was used as crosslinking agent. Dienophile named 11-maleimido-undecanoic acid was first synthesized and between this dienophile and commercial 3-(2-furyl) propanoic acid, the DA reaction was studied to determine DA and rDA reactions temperatures in the solid state. Then, an original modification method was employed to graft the two molecules onto the Lotader® poly(ethylene-co-glycidyl methacrylate) in one step procedure. The DA and rDA reactions between diene and dienophile grafted moieties are followed by FT-IR analysis on a thin film. Readily polymer network is synthesized and the cycle of DA and retro-DA reactions is repeatable with no significant polymer degradation.

1. Introduction

During the past 20 years, a growing interest has appeared with the application of the Diels–Alder (DA) reaction to macromolecular chemistry [1–7] and its possible thermal reversibility by retro Diels–Alder reaction (rDA) [8–10]. A particular diene/dienophile couple, known as furan/maleimide shows very interesting features via the Diels–Alder reaction [11]. Various macromolecular structures benefit from the DA and retro Diels–Alder (rDA) reactions, due to their versatility and simplicity. Gandini and coworker studies [12–14] have shown the feasibility of growing macromolecular chains thanks to Diels–Alder reaction with bifunctional diene and dienophile molecules. Goiti et al. [15,16] have demonstrated the reversibility of (styrene-co-furfurylmethacrylate) copolymer crosslinking with a bis-dienophile. In a different way, furan and maleimide copolymers [17,18] were also used to realize polymer networks without bis-dienophile molecules. Another procedure was adopted by several authors [19–22] with multifunctional maleimide and furan compounds. All these studies were conducted using solvents or liquid reagents, small molecules or sometimes model copolymers and the reactions were mostly followed by UV, FT-IR, ^{1}H NMR or DSC. The scope of this study is to synthesize a thermoreversible crosslinked commercial polyethylene having pendant furan and maleimide molecules. Furan and maleimide functions were grafted on the Lotader® (polyethylene-co-glycidyl-methacrylate) in one step by using a DA adduct obtained from cycloaddition between 3-(2-furyl)propanoic acid (Fac32) and the synthesized 11-maleimido-undecanoic acid (AMU) dienophile (Scheme 1). The relative ease of adduct formation and rDA cleavage of furan/maleimide moieties was used to modulate the properties of grafted polymer. Fac32 and AMU acids were particularly appropriate for the attachment on polymer with epoxy moieties. Herein, the polymer modification was conducted through epoxy-acid reactive extrusion.

The presence of a long alkyl chain on AMU also provides ample opportunity to perform the DA and rDA reactions between the attached groups in the modified polymer.

Studies of the rDA and DA reactions were performed by FT-IR spectroscopy for both DA adduct and modified copolymers. ^{1}H NMR analysis was not used because polyethylene was soluble at higher temperature and so, DA and rDA reactions are difficult to quantify at lower temperatures.

2. Experimental

2.1. Material and characterization

Maleic anhydrid (Merck, purity 95%, m.p. 51–54 °C) and undecanoic acid (Aldrich, purity 95%, m.p. 189–192 °C) were used as received.

Lotader® F0206, low density polyethylene-co-glycidyl methacrylate (PE-GMA) with 13.5% wt of GMA is a colorless random

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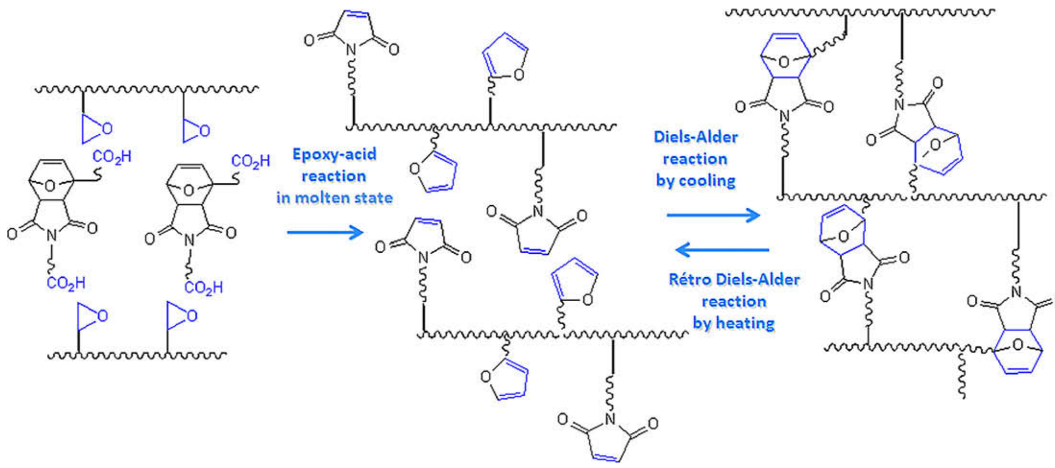


Scheme 1. Overall descriptive scheme of chemical reactions on the Lotader® (polyethylene-co-glycidylmethacrylate).

copolymer. It was kindly supplied by Arkema, France. Average molecular weight was estimated by SEC to be 135,000 g mol^{-1}, m.p.: 101 °C, FT-IR (thin film, cm^{-1}): 2930(CH), 1730(C=O), 1250(C—O epoxide), 1148(C—O ester), 1470(CH). ^{1}H NMR (250 MHz, TCE/C_6D_6, 365 K, ppm): 4.2 (d,1H,OCH), 3.8 (d,1H,OCH), 2.95 (m,1H, CH epoxide), 2.5 (m,1H,CH_2 epoxide), 2.36 (m,1H,CH_2 epoxide), 1–1.5 (m,CH_2 backbone), 0.9 (m,3H,CH_3).

3-(2-furyl)propanoic acid (Fac32) was purchased from Acros society and used as received. Purity 98%, m.p. 56 °C. FT-IR (KBr, cm^{-1}): 2700–3300(COOH), 2900(CH), 1700(C=O), 1595(C=C), 1506(C=C), 1221(C—O), 760(=CH), 600(=CH). ^{1}H NMR (250 MHz, Acetone, 298 K, ppm): 10.6 (s,1H,COOH), 7.4 (d,1H,CH furan ring), 6.2 (m,1H,CH furan ring), 6.1 (d,1H,CH furan ring), 2.9 (t,2H,CH_2), 2.6 (t,2H,CH_2).

The polymer modification was performed in a Minilab II, Haake rheomix CTW5 mini twin-screw extruder (with conical screws of 5/14 mm diameters and 109.5 mm in length) at 140 °C and a screw rotation rate of 130 rpm.

^{1}H NMR characterizations were performed on a Brucker Advance spectrometer at 250 MHz or 400 MHz with DMSO-d_6 (for the DA adduct) or $C_6D_4Cl_2$ (for polymers) as solvents and tetramethylsilane (TMS) as internal standard. FT-IR analysis were carried out on a Nicolet NEXUS Fourier Transform Infrared on KBr pellets for DA adduct and on a 50–80 μm thick film obtained at 140 °C under 180 bars for polymers. A SPECAC RS232 controller connected to a variable temperature sample cell was employed and Macros Basic 5.2 and OMNIC ESP 5.2 were used as acquisition softwares. In dynamic temperature conditions, the heating and cooling rates were 7.6° min^{-1} and 1.4° min^{-1}, respectively for all polymer samples.

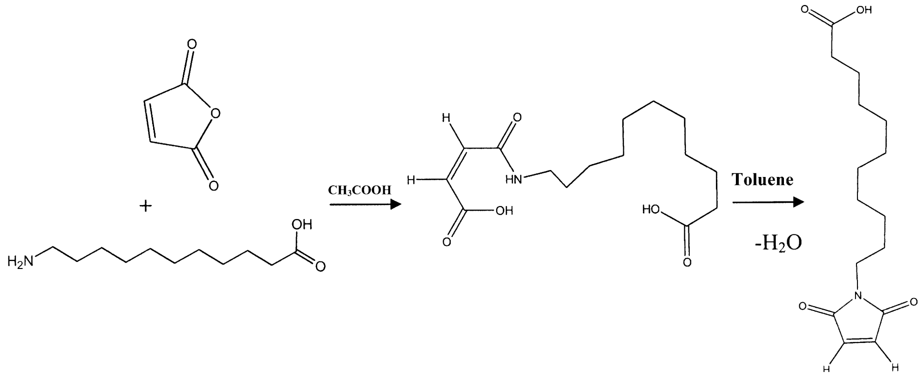
DSC analyses were carried out on TA Q10 Differential Scanning Calorimeter at heating and cooling rate of 2° min^{-1} or 10° min^{-1} under N_2 atmosphere.

For Steric Exclusion Chromatography (SEC) a Waters Alliance GPCV2000 apparatus equipped with styragel columns (at 140 °C) was employed with on-line refractive index and viscosimeter detectors. 1,2,4 trichlorobenzene was used as eluent with a 1 mL min^{-1} flow rate. Monodispersed polystyrene standards were used to obtain a calibration curve and estimate the molar weights.

2.2. Synthesis of 11-maleimido-undecanoic acid (AMU)

According to the reported method of Mantovani et al. [23], new reagent named 11-maleimido-undecanoic acid (AMU) was prepared from maleic anhydride and aminoundecanoic acid, as shown in Scheme 2. Indeed, to the best of our knowledge, the synthesis of AMU has not been reported in previous literature.

The maleic anhydride (5.00 g, 51 mmoles) was suspended in 70 mL of acetic acid at room temperature. A solution of aminoundecanoic acid (11.29 g, 63 mmoles) in 25 mL of acetic acid was added dropwise and the resulting solution was stirred at room temperature during 3 h. Then, the blend was heated to 115 °C. When the mixture became colorless, 50 mL of acetic acid were added and the solution was finally refluxed overnight. The mixture was cooled to room temperature and the solvent removed under reduced pressure. The brown residue was further dehydrated with



Scheme 2. Synthesis of 11-maleimido-undecanoic acid.

a Dean Stark apparatus in refluxing toluene during 24 h to close the hemi-ester. Purification by chromatography (CC, SiO_2, 70/30 CH_2Cl_2/ethyl acetate) gives the AMU dienophile (4.68 g, 17 mmoles, 34% yield, purity 86%) as a white solid. m.p. 88 °C. The structure of this dienophile was clearly identified by ^{1}H NMR with a resonance of ═CH maleimide proton at 6.86 ppm.

FT-IR (KBr, cm^{-1}): 2500–3300(COOH), 2900(CH), 1700(C═O), 1412(C—N), 830(═CH), 700(═CH).^{1}H NMR (250 MHz, Acetone, 298 K, ppm):10.4 (s,1H,COOH), 6.86 (s,2H,CH maleimide ring), 3.48 (t,2H,CH_2–N), 2.3 (t,2H,CH_2CO), 1.6 (m,4H,CH_2), 1.33 (m,12H,CH_2).

2.3. Synthesis of Fac32/AMU adduct

AMU and Fac32 were blended under stoichiometric conditions in an agate mortar at room temperature during 5 min. The solid mixture was stirred at 125 °C until melting before cooling to room temperature. The solid compound appeared from 113 °C. The resulting Diels–Alder adduct was washed with cold diethyl ether and ethyl acetate to afford a white powder with a 99% yield. m.p. 128 °C, IR (KBr, cm^{-1}): 2500–3300(COOH), 2900(CH), 1700(C═O). ^{1}H NMR (250 MHz, DMSO, 298 K, ppm): 12 (s,2H,COOH), 5.0 (s,1H,CHO), 3.0 (d,1H,CHC═O), 2.8 (d,1H,CHC═O), 2.17 (t,2H,CH_2CO), 1.46 (m,4H,CH_2), 1.21 (m,12H, CH_2).

2.4. Fac32/AMU adduct grafting onto Lotader® F0206

The Fac32/AMU adduct grafting reaction onto Lotader® F0206 is an epoxy-acid reaction between adduct acid functions and polymer epoxy groups.

Fac32/AMU modified copolymers were prepared as follows with an acid/epoxy stoechiometric ratio of 1.2/1. In a typical experiment, PE-GMA pellets were dried overnight at 90 °C to minimize the possibility of hydrolytic degradation. At first, 3 g were introduced into the extruder and after complete melting of the polymer, 2 g mixture of ground PE-GMA pellets and Fac32/AMU adduct was added. Temperature and torque were monitored during the experiments. Reactive mixing was extended for an additional period of 10 min before quenching the brown mixture in liquid nitrogen. Samples were purified by dissolution in hot dichlorobenzene followed by precipitation through the addition of an excess of petroleum ether. They were dried for 12 h at room temperature under vacuum and characterized by FT-IR and ^{1}H NMR spectroscopy.

m.p.: 94 °C, T_c: 77 °C, IR (thin film, cm^{-1}): 3500(OH), 1720(C═O), 1595(C═C furan), 1506(C═C furan), 700(═CH maleimide). ^{1}H NMR (400 MHz, $C_6D_4Cl_2$, 423 K, ppm): 6.31 (s,2H,CH of maleimide ring), 6.09 (s,1H,CH of furan ring), 5.87 (s,1H,CH of furan ring), 5.0 (m,1H,$CHCH_2OH$), 4.27 (s,1H,CH_2O), 3.96 (s,1H,CH_2O), 3.64 (s,2H,CH_2OH), 3.35 (t,2H,CH_2—N), 2.84 (d,2H,CH_2—C furan ring), 2.4–2.5 (m,2H,CH_2COO), 2.21 (m,2H,CH_2CH_2COO).

2.5. Study of DA and rDA reactions by FT-IR analysis

The DA and rDA reactions in Fac32/AMU adduct and modified polymers samples were studied by following the intensity (I) of the (C═C) furan (1505 cm^{-1}) and (═C—H) maleimide (700 cm^{-1}) absorption bands with temperature. A series of tests in the same conditions was used to estimate the measurement error ΔI (0.05). Two internal references (Iref) were used; one at 1700 cm^{-1}, (C═O absorption band for adduct with small molecules), the other at 3500 cm^{-1} (O—H modified polymer absorption band).

DA and rDA reactions progress was correlated with I_R and I_R^* respectively.

I_R and I_R^* are defined by:

	$I_R = \frac{(I/\text{Iref})\ \text{at}\ T}{(I/\text{Iref})\ \text{at}\ T_0}$	$I_R^* = \frac{(I/\text{Iref})\ \text{at}\ T - (I/\text{Iref})\ \text{at}\ T_0}{(I/\text{Iref})\ \text{at}\ T_0}$
with	T = measurement temperature	T = measurement temperature
	T_0 = initial temperature (140 °C)	T_0 = initial temperature (20 °C)
$I = I_{C=C}$ furan or $I_{=C-H}$ maleimide		

I_R and I_R^* were represented graphically versus time for isothermal conditions and versus temperature for dynamic conditions.

Therefore, if the DA reaction takes place during the sample cooling, the decrease of C═C (furan) and C═CH (maleimide) absorption bands intensity is expected and should induce I_R reduction. Otherwise, while heating the sample, I_R^* values should increase thanks to the rDA reaction.

3. Results and discussion

3.1. Synthesis of Fac32/AMU adduct and its Diels–Alder and retro-Diels Alder reactions

The ^{1}H NMR and FT-IR analysis indicate formation of a Diels–Alder adduct between AMU and Fac32 molecules (Figs. 1 and 2). For example, the peaks at δ = 6.86 and 7.4 ppm for protons (x) of maleimide moieties and proton (y) of furan moieties are absent in the ^{1}H NMR spectrum of the adduct (Fig. 1). A new signal at δ = 3 ppm corresponding to the hydrogen of the adduct bridge is observed. FT-IR analysis was performed by band integration according to the Beer–Lambert law, applicable for weakly absorbing species.

The FT-IR spectra (Fig. 2) support this result, showing no absorption band around 1600 and 1500 cm^{-1} for furan ring and 700, 830, 3100 cm^{-1} for maleimide ring, proving disappearance of the double bond of ring moieties.

Diels–Alder and retro-Diels–Alder reactions were studied with the Fac32/AMU model adduct for a better understanding of the thermal reactivity of these compounds. The ═C—H maleimide FT-IR absorption frequency at 700 cm^{-1} was measured to follow DA and rDA reactions at different temperatures. After an initial heating period from 20 to 120 or 140 °C, rDA reaction was followed in isothermal conditions and was represented by I_R^* intensity versus time (Fig. 3). These experiments clearly show that the rDA reaction starts at 120 °C with a faster reaction at 140 °C. Indeed, at 140 °C we can observe no important evolution while a significant I_R^* increase occurs at 120 °C up to 80 min.

I_R^* intensity increases and the curve approaches a horizontal asymptote. Maximum value of I_R^* was different at 120 and 140 °C, suggesting equilibrium with the DA reaction. The heating time was estimated at 11 min between 20 to 140 °C and the Fig. 3 shows that equilibrium state at 140 °C was established during the heating period. Besides, during the cooling, the Diels–Alder reaction between maleimide and furan moieties was observed [24].

Thermal behavior of Fac32/AMU adduct toward DA and mostly rDA shows interesting temperatures for applications with the Lotader® F0206 polymer. To apply the DA reversible reaction one needs to graft the adduct onto the polymer. The next section will specify the conditions for melt grafting of these molecules onto polymer.

3.2. Diene and dienophile grafting onto Lotader® F0206 polymer from Fac32/AMU adduct

An original one step procedure was used to introduce 11-maleimido-undecanoic acid (AMU) and 3-(2-furfuryl)propanoic

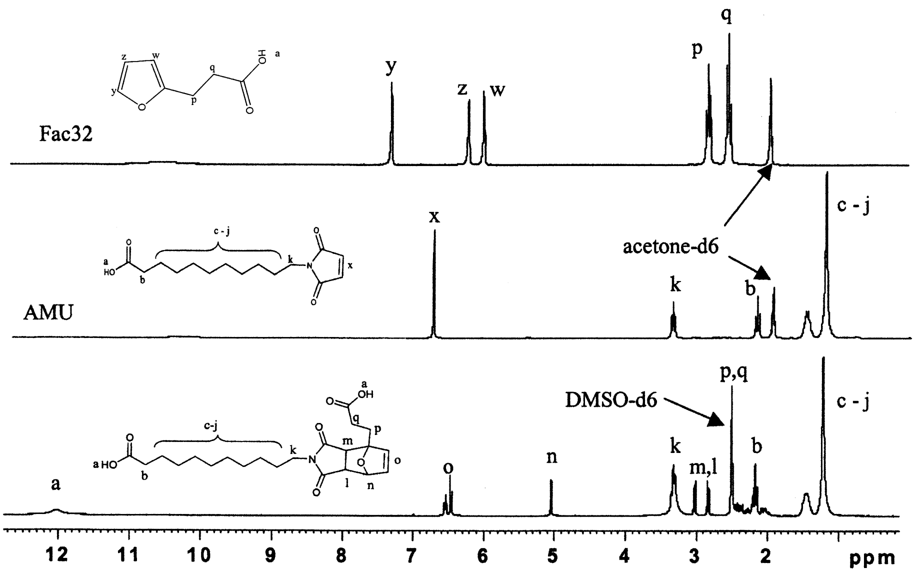


Fig. 1. 3-(2-furyl)propanoic acid (Fac32), 11-maleimido-undecanoic acid (AMU) and Diels Alder adduct ^{1}H NMR spectra.

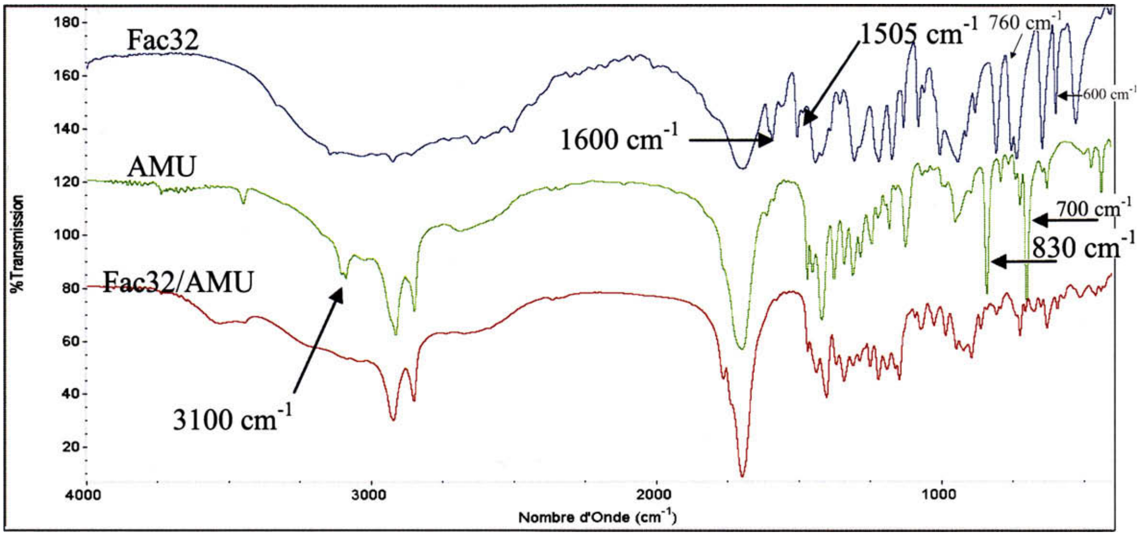


Fig. 2. FT-IR of 3-(2-furyl)propanoic acid (Fac32), 11-maleimido-undecanoic acid (AMU) and Fac32/AMU adduct.

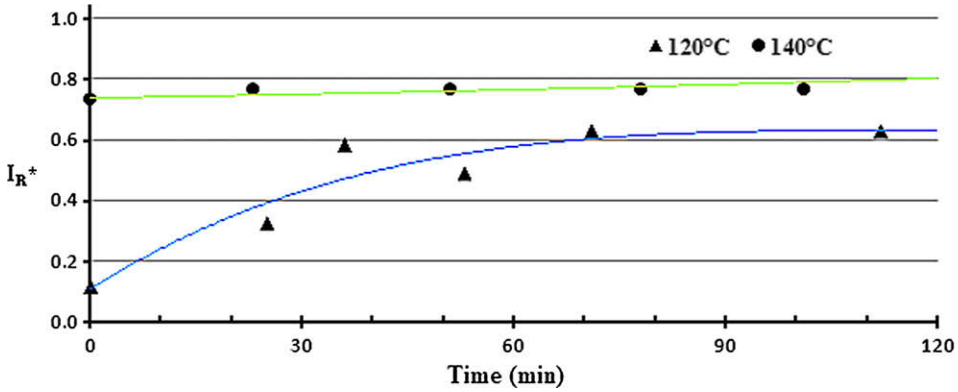


Fig. 3. I_R^* intensity of the =C—H maleimide (700 cm^{-1}) absorption band as a function of time for various isotherms (rDA reaction).

acid (Fac32) molecules in the melting polymer by using the Fac32/AMU adduct synthesized as described previously. The grafting of AMU and Fac32 molecules onto Lotader® F0206 through epoxy-acid chemical reaction has been performed in microextruder in short time.

In these conditions, we were able to avoid the inconvenient side reactions described in the literature. Indeed, maleimide double bond is known to be reactive at high temperature [25] especially in the presence of epoxy function as shown by Ashok Kumar et al. [26]. As many authors quoted in organic synthesis [27–29], the protection of dienophile maleimide double bond can be accomplished through a Diels–Alder reaction using furan as diene.

Fig. 4 shows the plots of torque versus time in extruder before and after addition of the Fac32/AMU adduct into polymer. Interestingly, addition of adduct caused a slight decrease of the torque and a major increase after 10 min of mixing due to the chemical grafting of Fac32 and AMU acids.

Fig. 5 illustrates the ^{1}H NMR spectra of Lotader® F0206 and the corresponding modified product. The spectrum of Lotader® F0206 displays characteristic peaks at 2.3–2.5 and 3 ppm related to epoxy moiety. The modified polymer presents additional peaks in the range of 5.87–6.09 ppm and 6.31 ppm which could be attributed to the CH of furan and maleimide moieties respectively. Simultaneously, the peaks around 2.4–2.5 and 3 ppm due to the epoxy function decrease and confirm the grafting of maleimide and furan onto the PE backbone. During the reaction, it is assumed that the epoxy groups react preferentially with the carboxyl rather than with the secondary hydroxyl issue of the epoxy ring opening [25,30–33]. The grafting yield was 84% with higher reactivity of the diene Fac32 (60%) compared to the dienophile AMU (40%).

Modification of the polymer was achieved at 140 °C in less than 15 min with a high conversion yield. The corresponding polymer film was subjected to FT-IR analysis to follow the DA and rDA reactions as a function of temperature.

3.3. Analysis of modified polymer films

In this section, we describe the evolution of DA and rDA reactions as a function of temperature by employing the same I_R^* and I_R units used to study the Fac32/AMU adduct.

Fig. 6 shows the I_R^* evolution of (=C—H) furan absorption band (1505 cm^{-1}) and (=C—H) maleimide absorption band (700 cm^{-1})

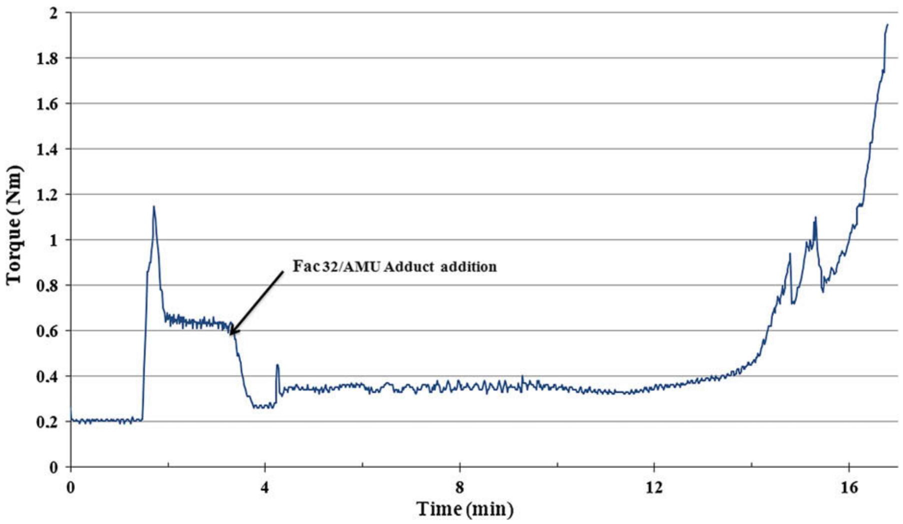


Fig. 4. Torque evolution versus time of 3-(2-furyl)propanoic acid (Fac32) and 11-maleimido-undecanoic acid grafting onto Lotader® polymer.

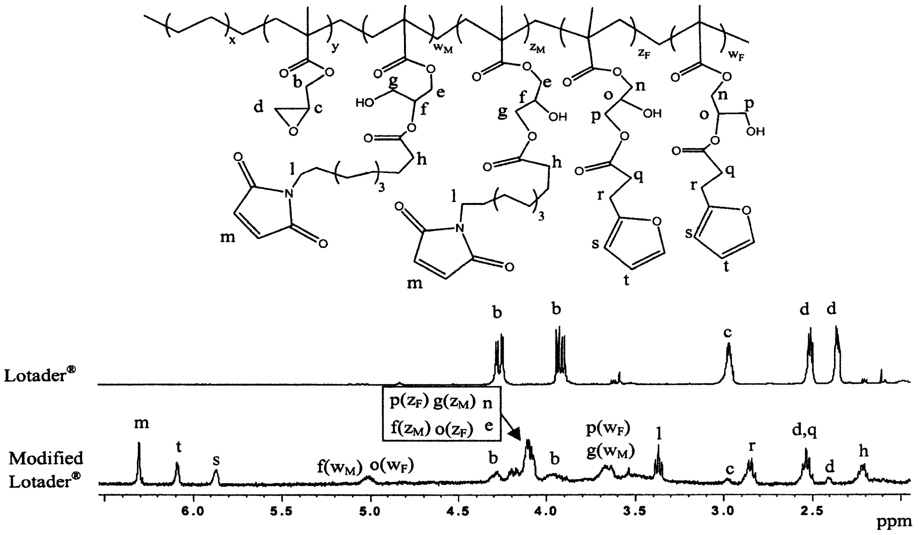


Fig. 5. ^{1}H NMR spectra of unmodified polymer and modified polymer.

while heating from 20 to 160 °C (the experiment takes approximately 20 min). The increase of the absorption bands intensity indicates the occurrence of retro DA reaction which demonstrates the regeneration of maleimide and furan moieties. The rDA reaction is significant at the temperature of 80 °C. However, at 94 °C, the modified polymer melts, and as a consequence polymer chains mobility is considerably increased. Thus, one can distinguish two slopes before and after this temperature for both wave numbers.

Fig. 7 depicts the evolution of both furan and maleimide absorption bands upon cooling at a rate of 1.4° min^{-1} from 140 °C to 40 °C. A few interesting features can be observed: I_R decrease occurs right from the start of the cooling for both wave numbers. The minimum value of 0.7 for (=C—H) maleimide absorption band is reached in 72 min. The DA reaction occurs immediately and in a larger extent when diene and dienophile molecules are grafted. A systematic I_R difference of 0.1 between furan and maleimide absorption bands reaches at the end of the reaction. This I_R difference can be attributed to Fac32/AMU grafting ratio previously observed with an excess of grafted furan functions leads to different I_R values for maleimide and furan functions.

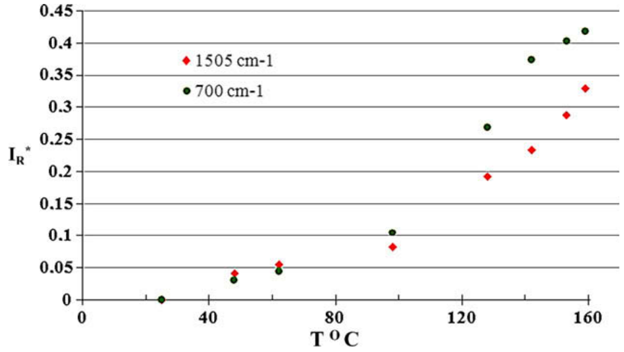


Fig. 6. I_R^* evolution of (=C—H) furan (1505 cm^{-1}) and (=C—H) maleimide (700 cm^{-1}) bands versus temperature for the modified polymer film (retro DA reaction).

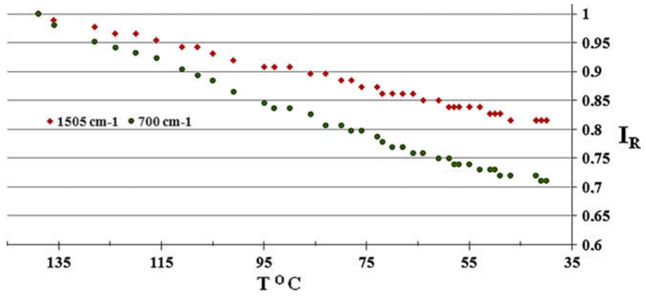


Fig. 7. I_R evolution of (=C—H) furan (1505 cm^{-1}) and (=C—H) maleimide (700 cm^{-1}) bands versus temperature (upon cooling) for the modified polymer (DA reaction).

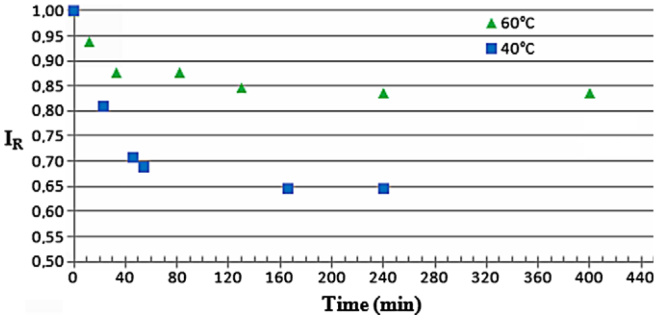


Fig. 8. I_R evolution versus time.

Decreasing of I_R in Fig. 7 is slightly slower below the crystallization temperature of the polymer (77 °C). So we can acknowledge the fact that if DA reaction is more favorable in molten polymer, it also seems possible below the crystallization temperature of the polymer.

3.4. Evolution of DA and rDA reactions with time

DA and rDA reactions (Figs. 8 and 9) were followed with time in isothermal conditions.

After an initial cooling period of 40 min from 140 °C to 60 °C (average cooling rate 2° min^{-1}) and of 75 min from 140 °C to 40 °C (average cooling rate 1.33° min^{-1}), samples were followed at 60 °C or 40 °C. Fig. 8 shows that I_R decreases until a constant value proving equilibrium is attained. Minimal I_R value is obtained for 40 °C, indicating that DA reaction is more important at this temperature.

Fig. 9 describes the evolution of I_R^* as a function of time.

As expected, I_R^* value at 120 °C is higher than at 80 °C or 60 °C as a consequence of the DA/rDA reaction equilibrium occurring at each temperature. Also, these results (at $T = 60$ °C or 80 °C) show that the rDA reaction is possible in the solid state of polymer.

To ensure the reversibility of DA and rDA reactions, polymers films were submitted to several cycles of heating (from 40 °C to 140 °C, average heating rate: 12° min^{-1}) and cooling (from 140 °C to 40 °C, average cooling rate: 3.4° min^{-1}). DA and rDA reactions were followed by I_R^* determination based on the (=CH) maleimide absorption band.

Fig. 10 displays the variations of maleimide I_R^* during 20 cycles (14 h) and shows the repeatability of these reactions with a small reactivity lost from the 6th cycle. The resultant polymeric material

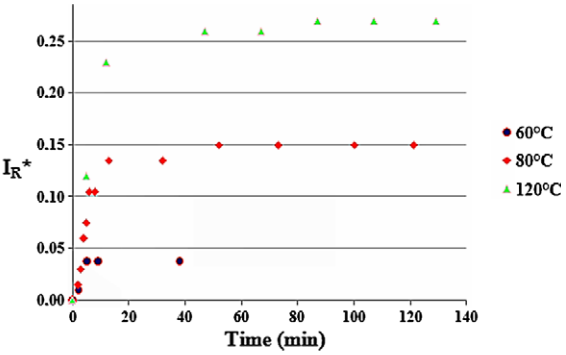


Fig. 9. I_R^* evolution versus time.

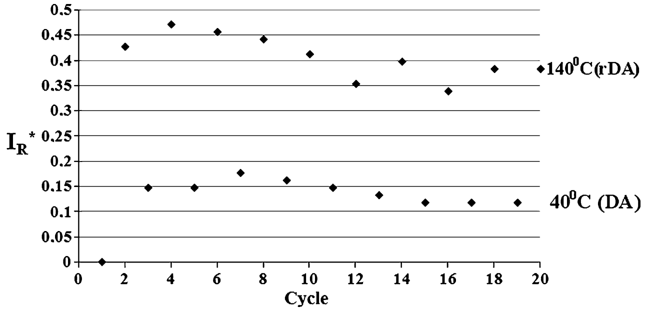


Fig. 10. I_R^* evolution for several cycles of DA (at 40 °C) and rDA (at 140 °C) reactions.

can be repeatedly mend and remend. At temperature above 140 °C, the linkages disconnect and then reconnect upon cooling. Thus it seems possible to break and rebuild a cross linked network several times with a good yield.

4. Conclusion

In search of thermally cleavable polymer, an original one step procedure was used to functionalize the Lotader® polymer in molten state by employing a Diels–Alder adduct. The DA adduct, obtained between 3-(2-furyl)propanoic acid as diene and the synthesized 11-maleimido-undecanoic acid, exhibited thermally reworkable features. The FT-IR analysis technique was applied to show DA and rDA reactions on the modified polymer film. Test proving the DA and rDA reactions reversibility was carried out on 20 cycles of heating and cooling and shows new potential applications of these materials.

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