

Reversibly Crosslinked Self-Healing PCL-Based Networks

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ABSTRACT: Poly(ϵ -caprolactone) (PCL)-based thermoreversible networks with self-healing properties were prepared through Diels–Alder (DA) and retro-DA reactions. Bis- or Tris-maleimide compounds and a series of copolymer(caprolactone-diene) PCL_XF_Y (X : degree of polymerization and Y : furan-average functionality) with Y between 2.4 and 4.9 were used. The successive sequences of formation and dissociation of polycaprolactone networks via DA and retro-DA reactions were observed repeatedly by dynamic mechanical analyses (DMA) and their gel-temperatures determined. The cross-linking densities, thermal properties, and thermal reversibility of the PCL_XF_Y/multimaleimide polymers have been modulated by the structure and functionalities of the used diene and dienophile moieties. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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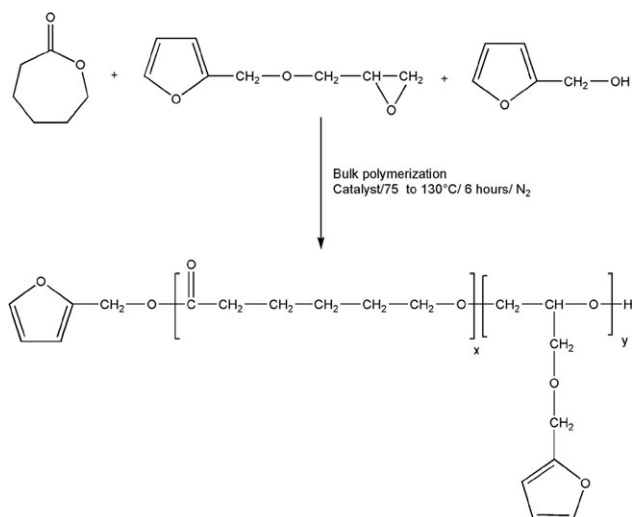
INTRODUCTION

Polycaprolactone (PCL) is a very attractive polymer due to its sustained biodegradability, low cost, and availability. Furthermore, PCL's physicochemical properties (semicrystallinity, hydrophobicity...) can be tuned easily through chemical modification or copolymerization with other monomers. The cross-linking of homo- and copolymers often leads to superior mechanical properties of these materials, such as high modulus and dimensional stability. Besides, during the last decade, several strategies for cross-linking of PCL derivatives have been used. Very recently, it was shown that PCL networks can exhibit excellent shape memory properties such as fixity and recovery ratios.^{1,2} So, these networks can display biodegradability, biocompatibility, shape memory and in some cases, recyclability. These advantages open up new perspectives for biomedical applications (degradable stents and implants, drug carrier matrices, hard and soft tissues engineering,) or for recyclability and reprocessing of crosslinked materials.

Several physical and chemical methods of PCL crosslinking have been reported in literature. The photo-crosslinking was one of the approaches used by Wang et al.³ to synthesize poly(ϵ -caprolactonefumarate) networks and to control their mechanical properties. Lendlein et al.⁴ have employed this method, among others, for the preparation of a family of oligo(ϵ -caprolactone)-co-glycolide)-dimethacrylate derived networks as controlled

release matrices. PCL networks were also synthesized by copolymerization with multifunctional monomers or prepolymers. Several interesting approaches were proposed by Albertsson et al.⁵ including the ring opening polymerization of the ϵ -caprolactone with co-monomer using advantageously a cross-linking agent of similar molecular structure as a bis- ϵ -caprolactone for degradable and biocompatible network formation in one-step.

The implementation of reversible chemical reactions of the “Dynamic Covalent Chemistry”⁶ that allows the connection and disconnection of components within a molecular architecture can lead, under well-defined conditions, to reversible networks. Diels–Alder (DA) is a well-known thermoreversible reaction.^{7,8} Polymer networks obtained from DA reactions are attractive because they can have both the benefits of the strong chemical networks and the thermal reversibility. Reversible Diels–Alder polymer networks from reactions between furan and maleimide moieties have been widely studied, especially during the last 5 years.^{9–21} It is easy to regulate the DA/retro DA equilibrium of reaction between temperatures lower than 100°C where Diels–Alder reaction proceeds and higher temperatures where the retro DA (rDA) reaction becomes dominant in solution as well as in the bulk state. DA polymer networks can be obtained from three different ways; first, from a mixture of a Bis-maleimide or a Bis- or Tris-furan coupling agent with a



Scheme 1. Synthesis in one step of (PCL_xF_y) copolymers.

complementary functionalized polymer^{14–16,22–24}; second, from a mixture of multifunctional maleimide and furan molecules^{10,12,18,25,26}; third, from a mixture of maleimide and furan functionalized polymers.^{19,27–29} The first two ways are the most common. To the best of our knowledge, only two teams have recently prepared PCL-based networks via DA reaction. Ishida et al.³⁰ have described the effects of the sequencing control of cross-linking reaction (via DA reaction) and crystallization on the structure and physical properties of the cross-linked polymers derived from furyl-telechelic poly(caprolactone) prepolymers. The effects of the electron density and of the strength of hydrogen bonding in the vicinity of furan on the equilibrium control of DA reaction were also highlighted. PCL-based DA networks have also been studied recently by Jérôme et al.^{1,2,31} Their studies have particularly focused on the syntheses of new DA networks derived from 4-arm star-shaped polycaprolactone bearing hydroxyl groups at the end of each arm and highlighted their shape-memory properties. The functionalization of the prepolymer by furan moieties or maleimide moieties was performed using two synthetic methods. One process used is relatively slow and the reactions were made in solution using two successive esterification reactions.^{1,2} A faster process without solvent using a condensation reaction was also used.³¹ The cross-linking via DA reaction was then achieved by a very slow cooling of a melted blend of end-functionalized prepolymers and a linker-agent. The shape-memory properties of (furan-maleimide) networks were evaluated by thermomechanical tests on at least four cycles and were compared with those (anthracene-maleimide) networks² or were studied with two different cross-linking densities.³¹

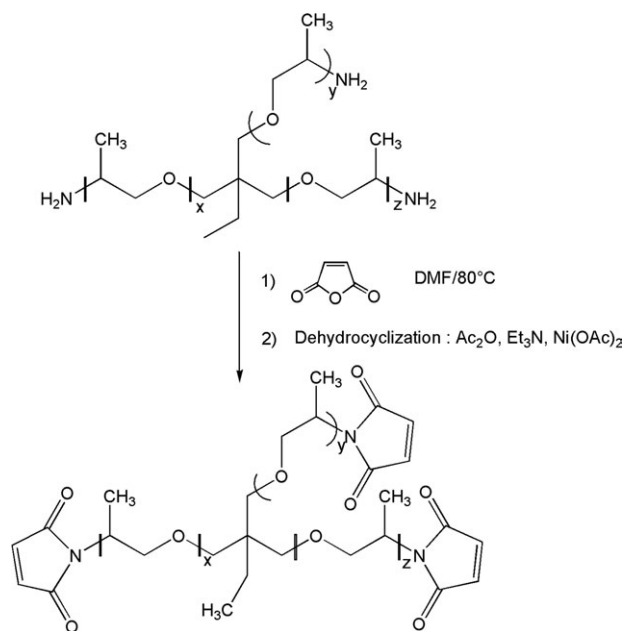
In this article, a one-pot original synthesis of PCL-based multifurane prepolymer was described by Ring-Opening copolymerization of the ϵ -caprolactone with furfuryl glycidyl ether. This new approach allowed an easy and rapid preparation of a series of copolymers (caprolactone-furan) for which it is possible to modulate continuously furan average functionality. It was chosen here to prepare PCL copolymers having furane functionalities between 2,4 and 4,9. Using these prepolymers, it is possible

to modulate the cross-linking density of DA networks on a wide range. These prepolymers do not contain urethane functions as obtained by Dubois et al.³¹ The urethane functions lead to supramolecular interactions that can mask the DA and rDA detection by rheological analysis. In the present study, the DA and rDA and the reversibility of networks obtained by coupling these copolymers with two multimaleimide linking-agents were characterized by several methods, especially by cyclic thermomechanical analysis. These analyses were used to clearly highlight the temperature ranges in which the DA reaction is predominant against the retro-DA reaction and their evolution with the cross-linking density of DA networks.

EXPERIMENTAL

Materials

The ϵ -Caprolactone (CL) (Solvay) was stirred over calcium hydride (CaH₂) for 48 h at room temperature and distilled under reduced pressure (0.2 mbar, 55°C). Pure ϵ -CL was stored over molecular sieves at room temperature. Furfuryl alcohol (FAL, Acros Organics, 98%) was fractionally distilled under reduced pressure. The middle portion was collected over anhydrous sodium sulfate, transferred thereafter to a high vacuum system and stored over CaH₂. Tin(II) bis(2-ethylhexanoate) [(Sn(Oct)₂, Aldrich, 95%] was purified twice by high vacuum distillation (0.2 mbar, 40°C). Furfuryl glycidyl ether (FGE, Georganics, 98%), Maleic Anhydride (Acros Organics, 98%), 1,6-diaminohexane (Aldrich, 98%) and polyoxypropylenetriamine (Jeffamine[®] T-403, C₆N₃H₁₇(C₃H₆O)₅, $M = 486 \text{ g mol}^{-1}$, Huntsman), 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD, Fluka, 98%) and Titanium (IV) butoxide (Ti(OBu)₄, Aldrich, 97%) were used as received.



Scheme 2. Synthesis of the Tris(maleimide)jeffamine T-403 (TrisM) with $x + y + z = 5$.

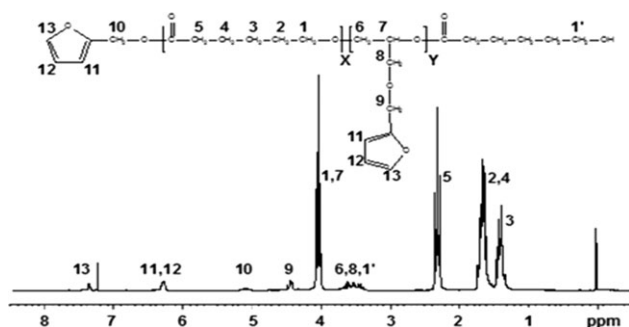


Figure 1. Typical chemical shifts for the spectrum $^1\text{H-NMR}$ in CDCl_3 after precipitation of (PCL_xF_y) copolymer obtained in the following conditions: 110°C , TBD as catalyst, $[\text{CL}]/[\text{FGE}] = 5$, $[\text{CL}]/[\text{TBD}] = 100$, $[\text{CL}]/[\text{FAL}] = 1000$.

Characterizations

$^1\text{H-Nuclear Magnetic Resonance}$ ($^1\text{H-NMR}$) spectra were recorded on a Bruker DRX250 spectrometer, 250 MHz at room temperature in CDCl_3 with tetramethylsilane (TMS) as an internal standard.

The thermal analyses of PCL-dienes and adducts were performed with a TA Q10 Differential Scanning Calorimeter. Polymer samples were weighed (2–3 mg) and placed into hermetic aluminum pans then heated under a nitrogen flow by two consecutive cycles at $10^\circ\text{C min}^{-1}$ from -80°C to 200°C . The melting (m.p.) and the crystallization (T_{crys}) temperatures were measured on the second cycle as the top values for the endothermic peak on heating and of the exothermic peak on cooling, respectively. The crystallization heat (ΔH_{crys}) was calculated by integration of the exothermic peak.

Thermogravimetric analyses (TGA) were performed on a thermal analysis instrument TGA-thermogravimetric analyzer. The samples (ca. 10 mg) were heated in alumina pans under nitrogen atmosphere (heating rate: $10^\circ\text{C min}^{-1}$, temperature range: $35\text{--}700^\circ\text{C}$). The gas flow rate was 80 mL min^{-1} .

The molecular weights and molecular weight distributions of (PCL_xF_y) copolymers were derived with a Waters 717 plus Gel Permeation Chromatograph, equipped with an auto sampler, styragel columns, 100, 200, 300 Å, aligned in series, a refractive-index and a light scattering detector. Tetrahydrofuran (THF) was used as eluent with a flow rate of 1 mL min^{-1} .

Dynamic Mechanical Analyses were performed with a TA Instruments DMA. The instrument was set up with 25 mm

parallel-plate geometry and the experiments were conducted in oscillatory mode under room pressure in the frequency range of $0.1\text{--}100\text{ rad s}^{-1}$ at constant temperature and at a frequency equal to 1 rad s^{-1} on heating up to 150°C then cooling down to 60°C , with a cooling and heating rate = 1°C min^{-1} . A previous determination of the linear viscosity field was performed in order to define the frequency of work (1 rad s^{-1}).

Synthesis of Polycaprolactone-dienes (PCL_xF_y)

Copolymerizations of the $\epsilon\text{-CL}$ with FGE by Ring-Opening Polymerization (ROP) under different conditions were studied in the presence of $\text{Sn}(\text{Oct})_2$, TBD or $\text{Ti}(\text{OBU})_4$ as catalysts and FAL as a chain limiting agent (Scheme 1). Batch syntheses (40 g) were made in a dry nitrogen atmosphere in a 250 mL glass reactor (90 mm diameter) with a three necked steel cover. A steel anchor stirrer operating with a RW 28 W IKA motor at 120 rpm, a condenser and a T-type thermocouple probe were fixed to the cover. Monomer $\epsilon\text{-Caprolactone}$ was fed to the reactor with appropriate amount of FGE, catalyst, and FAL. The molar ratio $[\epsilon\text{-CL}]/[\text{FGE}]$ was varied between 2 and 20 with the following values 2, 5, 10, and 20. Molar ratios $[\epsilon\text{-CL}]/[\text{catalyst}]$ and $[\epsilon\text{-CL}]/[\text{FAL}]$ were kept constants at 100 and 1000, respectively. The reaction was carried out at four different temperatures between 40 and 130°C for 6 hours. After copolymerization, the crude product was cooled at room temperature, dissolved in chloroform and precipitated in an excess of cold ethanol. After two cycles of this process, the resulting polymer was dried under vacuum at room temperature for 48 h.

Synthesis of 1,6-Bis(maleimide) Hexane (BisM)

The 1,6-Bis(maleimide) hexane was obtained following a previously described procedure³² from the reaction between 1,6-diaminohexane and an excess of maleic anhydride in solution in DMF for 30 min, at 90°C . In a second step, the dehydration between acid and amide was obtained in the presence of acetic anhydride, nickel (II)-acetate and triethylamine. After cooling, the resulting brown precipitate was filtered several times and washed with water before drying. Pale yellow crystals were obtained; m.p. 136°C . They are thermally stable up to 170°C . The reaction yield was 73.2% (In literature, the yields are much lower). $^1\text{H-NMR}$ (250 MHz, CDCl_3), δ (ppm) = 6.7 (s, 4H, $-\text{CH}=\text{CH}-$), 3.5 (t, 4H, $\text{N}-\text{CH}_2$), 1.6 (m, 4H, CH_2), 1.3 (m, 4H, CH_2). Maleimide average functionality, $f(\text{BisM})/^1\text{H-NMR} = 1.9$. $M = 277.2\text{ g mol}^{-1}$.

Synthesis of Tris(maleimide) Jeffamine T-403 (TrisM)

The Tri-maleimide synthesis from jeffamine[®] T-403 was developed in our laboratory (Scheme 2).³³ The procedure was slightly different from those previously reported for the

Table I. Effect of the Catalyst on the Copolymerization of $\epsilon\text{-CL}$ with FGE in Bulk at $T = 110^\circ\text{C}$ for 6 h, $[\text{CL}]/[\text{FGE}] = 5$, $[\text{CL}]/[\text{FAL}] = 1000$, and $[\text{CL}]/[\text{Cat}] = 100$

Catalyst	M_n^a (g mol^{-1})	M_w/M_n	f_{furan}^b	DPn^b	PCL_xF_y	m.p. ^c ($^\circ\text{C}$)	T_{crys} ($^\circ\text{C}$)	ΔH_{crys} (J g^{-1})	T_{TGA} (5%) ($^\circ\text{C}$)
$\text{Sn}(\text{Oct})_2$	6283	1.16	1.6	54.3	$\text{PCL}_{52.7}\text{F}_{1.6}$	49.5–53.8	24.5	57.6	288
$\text{Ti}(\text{OBU})_4$	9028	1.40	0	79.0	$\text{PCL}_{79}\text{F}_0$	54.1	29.5	65.7	267
TBD	6633	1.25	4.9	56.8	$\text{PCL}_{51.9}\text{F}_{4.9}$	40.9–49.0	14.1	51.0	338

^aDetermined by SEC, ^bDetermined from $^1\text{H-NMR}$ and SEC data on copolymers after precipitation, ^cEndotherm with two maxima.

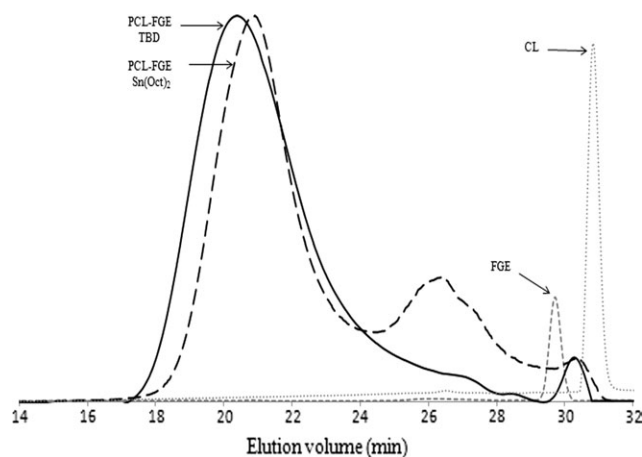


Figure 2. SEC spectra of crude (PCL_xF_y) copolymers with TBD or Sn(Oct)₂ as catalyst, 110°C, 6 h, [CL]/[FGE] = 5, [CL]/[FAL] = 1000, [CL]/[TBD] = 100.

synthesis of the Tris-maleimide from Tris(2-aminoethyl)-amine.^{32,34} After dehydrocyclization and the removal of reactant residues and solvents, a viscous liquid was obtained. The reaction yield was 91%. The product was thermally stable up to 340°C, ¹H-NMR (250 MHz, CDCl₃), δ (ppm) = 6.6 (d, 6H, -CH = CH-), 4.3 (m, 3H, N-CH-), 3.8 (t, 5H, N-CH-CH₂-O), 3.6 (t, 5H, O-CH-CH₂-O), 3.5 (s, 3H, O-CH-CH₂-O), 3.3 (m, 6H, C-CH₂-O), 1.3 (q, 2H, -CH₂-CH₃), 1.2 (d, 30H, -CH-CH₃), 1.1 (t, 3H, -CH₂-CH₃). Maleimide average functionality, $f(\text{TrisM})/{}^1\text{H-NMR} = 2.55$. $M = 729 \text{ g mol}^{-1}$.

Synthesis of (PCL_xF_y/BisM) and (PCL_xF_y/TrisM)Diels–Alder Adducts

PCL-dienes and multimaleimide with molar stoichiometry (furan/maleimide = 1/1) were mixed in bulk at 140°C typically during 15 min. A homogeneous blend was obtained. The oven temperature was then gradually decreased (0.3°C min⁻¹) to 40°C and maintained constant at 40°C for 12 h.

The DA conversion rate can be considered as a gel-point conversion rate (12) and thus can be predicted by Macosko-Miller equation³⁵:

$$p_g = (r \times (1 - f(\text{furan}))(1 - f(\text{Maleimide}))^{-1/2}$$

where p_g is the gel-point conversion rate via DA reaction, r is the stoichiometric ratio, here $r = 1$, $f(\text{furan})$, and $f(\text{Maleimide})$ are the average functionalities for the furan and maleimide compounds, respectively (determined by ¹H-NMR analysis).

Table II. Effect of the Temperature on the Copolymerization of ϵ -CL with FGE in Bulk for 6 h with [CL]/[FGE] = 5, [CL]/[FAL] = 1000 and [CL]/[TBD] = 100

Temperature (°C)	M_n^* (g mol ⁻¹)	M_w/M_n	f_{furan}^a	DPn ^b	PCL _x F _y	m.p. ^c (°C)	T_{crys} (°C)	ΔH_{crys} (J g ⁻¹)	T_{TGA} (5%) (°C)
75	4552	1.27	0.9	39.5	PCL _{38.6} F _{0.9}	51.4–55.4	24.3	54.0	337
110	6633	1.25	4.9	56.8	PCL _{51.9} F _{4.9}	40.9–49.0	14.1	51.0	1338
130	7000	1.71	5.2	59.7	PCL _{54.5} F _{5.2}	44.3–50.3	21.8	54.4	343

^aDetermined by SEC, ^bDetermined from H-NMR and SEC data on copolymers after precipitation, ^cEndotherm with two maxima.

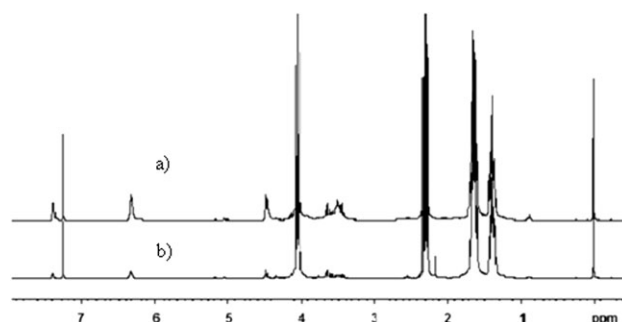


Figure 3. ¹H-NMR spectra in CDCl₃ before (a) and after (b) precipitation of (PCL_{52.7}F_{1.6}) copolymer obtained in presence of Sn(Oct)₂.

The cross-linking density of DA networks was characterized by the cross molecular weight between entanglements, M_c (kg mol⁻¹), calculated according to the equation³⁶:

$$M_c = (G'/\rho RT)^{-1}$$

where ρ (kg m⁻³) is the volumic mass of PCL ($\rho = 1160 \text{ kg m}^{-3}$)³⁷, R is the gas constant 8.314 J.(mol K)⁻¹, T is the temperature (K), and G' (Pa) is the storage modulus at 1 rad s⁻¹.

RESULTS AND DISCUSSION

Synthesis and Characterization of Furan Functionalized Polycaprolactone (PCL_xF_y)Copolymers

A one-step synthesis was used to prepare new copolycaprolactones with pendant diene functional groups and sufficient functionality to react with a multimaleimide and to obtain DA polymer networks. Several series of copolymers of FGE and ϵ -caprolactone were synthesized by ring opening copolymerization in the melt using a catalyst and FAL as chain limiting agent as illustrated in Scheme 1. The effects of the catalyst type, of temperature and of the [CL]/[FGE] molar ratio were investigated in order to obtain a maximum ϵ -CL conversion and efficient lactone epoxy copolymerization.

The structure of (PCL_xF_y) copolymers was determined from the ¹H-NMR spectra. A typical spectrum is given in Figure 1. The peaks at $\delta = 7.4$ and 6.3 ppm were assigned to the protons of furan ring, $\delta = 4.5$ and 3.6–3.3 ppm correspond to the protons in open FGE moities. The presence of the FAL can be highlighted by the methylene protons at $\delta = 5.1$ ppm. Methylene groups of the PCL were also identified.

Table III. Effect of the Molar Ratio CL/FGE on Copolymerization of ϵ -CL with FGE in Bulk at 110°C for 6 h with [CL]/[FGE]=20, 10, 5 et 2, [CL]/[FAL] = 1000, [CL]/[TBD] = 100

[CL]/[FGE]	M_n^a (g mol ⁻¹)	M_w/M_n	f_{furan}^b	DPn ^c	PCL _x F _y	m.p. ^c (°C)	T_{crys} (°C)	ΔH_{crys} (J g ⁻¹)	T_{TGA} (5%) (°C)
20	8631	1.37	2.4	774.8	PCL _{72.4} F _{2.4}	50.3–54.5	26.3	66.9	294
10	7705	1.27	3.8	66.1	PCL _{62.3} F _{3.8}	46.9–52.6	22.2	60.3	302
5	6633	1.25	4.9	56.8	PCL _{51.9} F _{4.9}	40.9–49.0	14.1	51.0	338
2	3696	2.32	2.9	31.5	PCL _{28.6} F _{2.9}	40.5–48.3	15.2	59.5	369

^aDetermined by SEC, ^bDetermined from ¹H-NMR and SEC data on copolymers after precipitation, ^cEndotherm with two maxima.

The conversion rate of the ϵ -CL into copolymer was calculated from spectra of the crude products according to the equation:

$$\text{Monomer conversion (\%)} = \frac{A_{\text{Csp2-CH2-(PCL-dienes)(2.3)}}}{(A_{\text{Csp2-CH2-(PCL-dienes)(2.3)}} + A_{\text{Csp2-CH2-}\epsilon\text{-CL(2.6)}})} \times 100$$

where $A_{\text{Csp2-CH2-(PCL-dienes)}$ (2.3 ppm) and $A_{\text{Csp2-CH2-}\epsilon\text{-CL}}$ (2.6 ppm) are the methylene protons areas of the PCL and the ϵ -CL, respectively. In the $A_{\text{Csp2-CH2-}\epsilon\text{-CL}}$ value, the contribution of the epoxy methylene from FGE residue was taken into account.

A high conversion was reached at the complete disappearance of the peaks (2.6 ppm) of the methylene protons in position 5 from ϵ -CL and epoxy methylene protons from FGE. With TBD as catalyst and the molar ratios [ϵ -CL]/[FGE] = 5, [ϵ -CL]/[TBD] = 100, [ϵ -CL]/[FAL] = 1000, at 110°C under nitrogen, the conversion of ϵ -CL reaches 99% after 6 h of reaction time and a maximum value (>99%) after 24 h.

The polymerization degree (DPn) and the furan average functionality (f_{furan}) of (PCL_xF_y) copolymers were determined from ¹H-NMR and SEC analysis according to the following equations:

$$\text{DPn} = X + Y$$

$$f(\text{furan}) = Y = Z + Z'$$

where X is the ϵ -CL moieties number, Z , the FGE moieties number and Z' , the FAL moieties number.

X , Z , and Z' are calculated from the average molecular weight (M_n) of (PCL_xF_y) copolymer, measured by SEC and the ratio $X/(Z + Z')$, derived from pure polymers ¹H-NMR analysis:

$$M_n = XM_{\text{CL}} + ZM_{\text{FGE}} + Z'M_{\text{FAL}}$$

Table IV. Thermal Properties of Adducts with Bis-maleimide and Tris-maleimide

[CL]/[FGE]	With BisM						With TrisM			
	f_{furan}	PCL _x F _y	m.p. (°C)	T_{crys} (°C)	ΔH_{crys} (J g ⁻¹)	T_{TGA} (5%) (°C)	m.p. (°C)	T_{crys} (°C)	ΔH_{crys} (J g ⁻¹)	T_{TGA} (5%) (°C)
20	2.4	PCL _{72.4} F _{2.4}	48–52.4	22.8	58.8	353	46.5–51.8	19.6	50.2	364
10	3.8	PCL _{62.3} F _{3.8}	46.4–51.3	22.3	51.3	323	44.9–50.1	17.9	55.3	370
5	4.9	PCL _{51.9} F _{4.9}	44.0–47.5	13.8	45.6	212	41.3–46.3	10.7	43.7	310
2	2.9	PCL _{28.6} F _{2.9}	41.9–48.5	12.9	50.8	236	42.4–48.5	15.2	52.3	357

$$X/(Z + Z') = \frac{A_{\text{Csp2-CH2-(PCL-dienes)(2.3)}}}{A_{\text{Csp2-H-FGE}} + A_{\text{Csp2-H-FAL(6.3)}}}$$

$$Z'/(Z + Z') = \frac{A_{\text{Csp2-CH2-FAL(5.1)}}}{A_{\text{Csp2-H-FGE}} + A_{\text{Csp2-H-FAL(6.3)}}}$$

where $A_{\text{Csp2-CH2-(PCL-dienes)}$ (2.3 ppm), $A_{\text{Csp2-H-FGE}} + A_{\text{Csp2-H-FAL}}$ (6.3 ppm), $A_{\text{Csp2-CH2-FAL}}$ (5.1 ppm) are the protons' peak areas of PCL, FGE, and FAL moieties, respectively. $M_{\epsilon\text{-CL}}$, M_{FGE} , and M_{FAL} are the molar weights of ϵ -CL, FGE, and FAL, respectively.

Effect of Catalyst Type. The effect of three catalysts (Sn(Oct)₂, Ti(OBu)₄, TBD) was investigated on the (PCL_xF_y) copolymers furan functionality and the degree of polymerization. Sn(Oct)₂ is a frequently used polymerization initiator for ROP of various lactones.^{38–40} The alcoxide metal, Ti(OBu)₄, was also commonly used in copolymerization of the ϵ -CL with adipic acid, hexan-1,6-diol, and pentaerythritol.⁴¹ The TBD has been recently recognized as a metal-free catalyst very prone to control the polymerization of lactide by dual monomer–alcohol activation.⁴² Table I shows the characteristics of the (PCL_xF_y) copolymers obtained in the presence of the different catalysts.

With Ti(OBu)₄, the copolymerization did not occur under the chosen experimental conditions. The ¹H-NMR spectrum of the resulting product and the thermal properties were identical to that of the homopolymer PCL. In the presence of TBD or Sn(Oct)₂, (PCL_xF_y) copolymers with smaller mass were obtained. Their melting points were close, their crystallization temperature (T_{crys}) and crystallization enthalpy variation (ΔH_{crys}) are slightly below those of the synthesized PCL in the presence of FAL and TBD, without FGE ($M_n = 12,600$ g mol⁻¹, m.p. = 53.0°C, $T_{\text{crys}} = 27.3$ °C, $\Delta H_{\text{crys}} = 64.1$ J g⁻¹). The thermal stability of copolymers prepared with TBD was higher than those of the copolymers prepared with the other catalysts. This

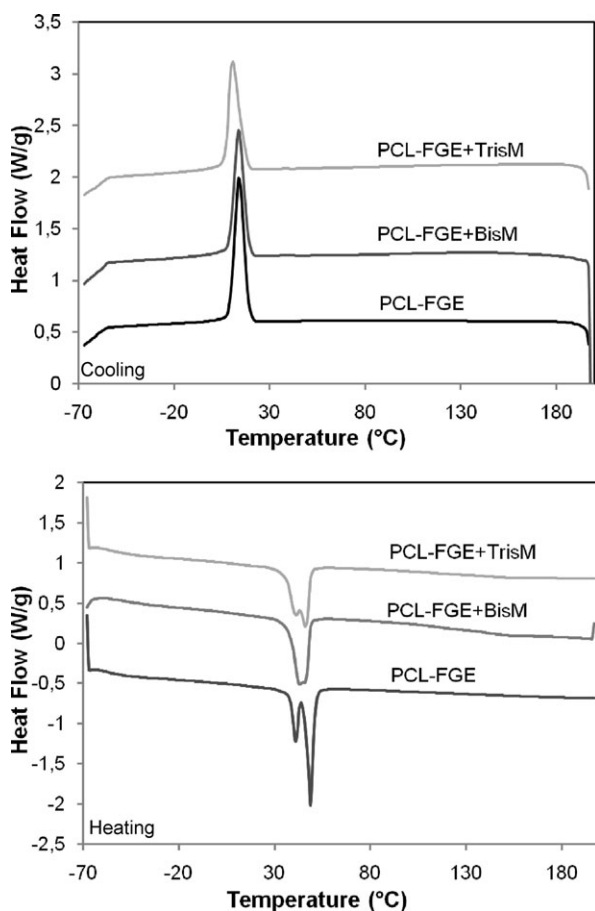


Figure 4. DSC curves of $(PCL_{51.9}F_{4.9})$ copolymer. Solid black line: without linker-agent, point gray line: with Bis-maleimide, short gray line: with Tris-maleimide. (a) DSC cooling curve, (b) DSC heating curve.

result can be explained by a greater furan rate; the rate of furan is three times as great in presence of TBD than with $Sn(Oct)_2$.

Figure 2 presents the SEC curves of (PCL_xF_y) copolymers catalyzed by TBD and $Sn(Oct)_2$, and the starting reagents, caprolactone and furfuryl glycidyl ether. The use of TBD allows the synthesis of a crude copolymer with relatively high molar weight.

Table V. Solubility Test of Adducts with Bis-maleimide and Tris-maleimide at Room Temperature in THF

PCL_xF_y	With BisM Rate of solubility ^a (%)	With TrisM Rate of solubility ^a (%)
$PCL_{72.4}F_{2.4}$	93.2	58.6
$PCL_{62.3}F_{3.8}$	43.8	34.0
$PCL_{51.9}F_{4.9}$	25.2	18.7
$PCL_{28.6}F_{2.9}$	37.6	28.8

^aRate of solubility = $[(\text{initial adduct weight} - \text{dried adduct weight}) / (\text{initial adduct weight})] \times 100$.

After 6 h of reaction at 110°C , the FGE totally disappeared. In the case of $Sn(Oct)_2$, a bimodal distribution was observed. $^1\text{H-NMR}$ spectra of this copolymer before and after purification (precipitation in ethanol in order to eliminate small polymer chains) were shown in Figure 3. The peaks corresponding to FGE disappeared ($\delta = 6.3, 4.5, 3.6\text{--}3.3$ ppm). So, in the presence of $Sn(Oct)_2$, the FGE is preferentially copolymerized with small chains.

According to these results, TBD is an efficient catalyst allowing the incorporation of FGE in the PCL chain without excessively reducing its length. It will be used in the next parts of the study.

Effect of the Temperature. The copolymerization of $\epsilon\text{-CL}$ with FGE was performed in the presence of TBD between 40 and 130°C in order to increase the degree of polymerization. At 40°C , no copolymerization was observed. The results at 75, 110, and 130°C are presented in Table II.

As expected, the degree of polymerization of the $\epsilon\text{-CL}$ increased with temperature.⁴³ At 75°C , the furan average functionality was insufficient ($f(\text{furan}) < 2$). The maximal furan average functionality was achieved at higher temperatures. Since this value is almost the same at 110 and 130°C , the lowest temperature was chosen for further tests to avoid side reactions.

Effect of the Molar Ratio $[CL]/[FGE]$. The effect of the molar ratio CL/FGE on the furan average functionality and the degree of copolymerization of the (PCL_xF_y) was also investigated with TBD as catalyst at 110°C . The initial molar ratios $[CL]/[FGE]$

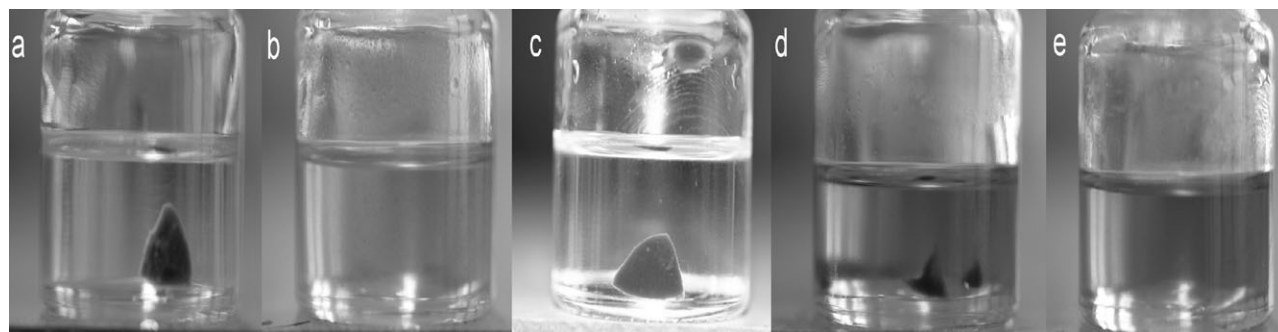


Figure 5. Tests of thermally responsive behavior of cross-linked $PCL_xF_y/Tris$ -maleimide adducts. (a) Cross-linked $PCL_{72.4}F_{2.4}/TrisM$ (Polymer in DMSO: 25°C , 1 h, insoluble), (b) Cross-linked $PCL_{72.4}F_{2.4}/Tris$ (Polymer in DMSO: 90°C , 1 h, soluble), (c) Cross-linked $PCL_{51.9}F_{4.9}/TrisM$ (Polymer in DMSO: 25°C , 1 h, insoluble), (d) Cross-linked $PCL_{51.9}F_{4.9}/TrisM$, (Polymer in DMSO: 90°C , 2 h, partially soluble), (e) Cross-linked $PCL_{51.9}F_{4.9}/TrisM$ (Polymer in DMSO: 110°C , 1 h, soluble).

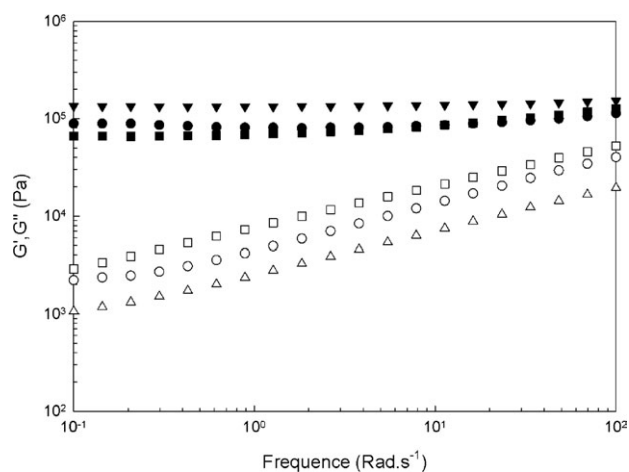


Figure 6. G' and G'' for $(PCL_xF_y)/Bis$ -maleimide adducts versus frequency at 60°C. G' : ● PCL_{28.6}F_{2.9}; ▼ PCL_{51.9}F_{4.9}; □ PCL_{62.3}F_{3.8}. G'' : ○ PCL_{28.6}F_{2.9}; △ PCL_{51.9}F_{4.9}; □ PCL_{62.3}F_{3.8}.

were chosen between 2 and 20. As shown in Table III all the obtained (PCL_xF_y) copolymers had a furan average functionality higher than 2. The mol % of FGE incorporated into the copolymer increased up to about 9% for $[CL]/[FGE] = 5$ and 2. With this last ratio the (PCL_xF_y) copolymer had a relatively low molar mass. Considering that a higher amount of FGE during copolymerization leads to an increase of the quantity of FGE in the copolymer and at the same time to a decrease of the molar mass of the copolymer, a compromise position concerning the FGE concentration was taken.

As was previously observed, the thermal stability of copolymers depends on the rate of incorporated FGE; a better thermal stability was obtained with higher furan rate. We can observe that when the number of furan functions increases, melting temperature, crystallization temperature, and crystallization enthalpy variation decrease. Furthermore, crystallinity decreases as well.

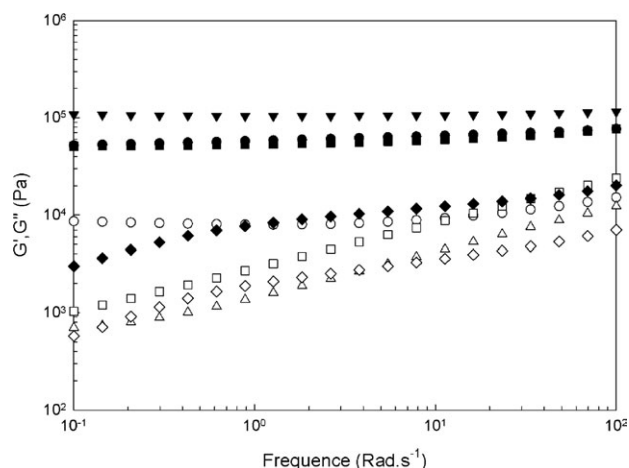


Figure 7. G' and G'' for $(PCL_xF_y)/Tris$ -maleimide adducts versus frequency at 60°C. G' : ● PCL_{28.6}F_{2.9}; ▼ PCL_{51.9}F_{4.9}; □ PCL_{62.3}F_{3.8}; ◆ PCL_{72.4}F_{2.4}. G'' : ○ PCL_{28.6}F_{2.9}; △ PCL_{51.9}F_{4.9}; □ PCL_{62.3}F_{3.8}; ◇ PCL_{72.4}F_{2.4}.

Table VI. Network Properties of Adducts with Bis-maleimide

PCL_xF_y	$X_{DA}(\%)$ Th	G'^a (Pa)	M_c^b (g/mol)	M_c/M_n
PCL _{72.4} F _{2.4}	89.1	-	-	-
PCL _{62.3} F _{3.8}	63.0	69,000	46,554	6
PCL _{51.9} F _{4.9}	53.4	133,000	24,140	4
PCL _{28.6} F _{2.9}	76.5	80,000	40,160	11

Synthesis and Characterization of $(PCL_xF_y/BisM)$ and $(PCL_xF_y/TrisM)$ Adducts

The Diels–Alder adducts were prepared after slow cooling of molten mixtures between the (PCL_xF_y) copolymers in Table III and the maleimide coupling agent (BisM or TrisM). Their thermal and thermomechanical properties were investigated. Usual and thermomechanical techniques were also used to highlight and to characterize the Diels–Alder reactions (DA and rDA).

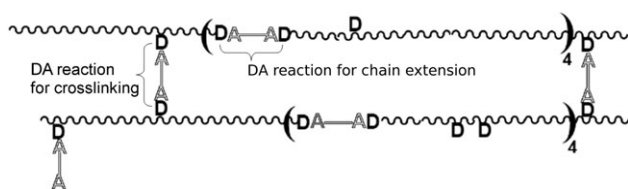
Thermal Properties

The DA adducts' thermal properties are shown in Table IV. It was expected that the degradation temperature of adducts would be higher than the rDA temperature, and so adducts' thermal stability should be similar to that of initial copolymers. In fact, differences were observed; the polymers' thermal stability after the DA reaction with maleimide is either superior (with Tris-maleimide) or inferior (with Bis-maleimide) to that measured for these initial copolymers. These differences can be assigned to the degradation of coupling agents. As already observed by Karateev et al.,⁴⁴ the thermal stability of DA networks with furfuryl glycidyl ether is overall higher than those of other furan derivative networks like those with furfuryl methacrylate.⁴⁵ As shown in Figure 4 for $(PCL_{51.9}F_{4.9})/BisM$ or TrisM adducts, the semicrystalline character was preserved. The melting and crystallization enthalpies of adducts were slightly lower than those of parent copolymers. The melting peak decrease, especially at the second endotherm, can be assigned to DA reaction between FGE rich copolymer blocks and linking-agents. On the other side, no other transition was observed at higher temperatures. Tests were also carried out with a slower heating without more significant results. Thus, in this case, the DSC analysis did not allow the observation of the rDA reaction as previously shown on different amorphous networks by Liu and Hsieh,¹⁰ Tian et al.,⁴⁶ or Canadell et al.⁴⁷

Table VII. Network Properties of Adducts with Tris-maleimide

PCL_xF_y	$X_{DA}(\%)$ Th	G'^a (Pa)	M_c^b (g/mol)	M_c/M_n
PCL _{72.4} F _{2.4}	67.9	8,000	401,606	46
PCL _{62.3} F _{3.8}	48.0	53,000	60,606	8
PCL _{51.9} F _{4.9}	40.6	168,000	19,120	3
PCL _{28.6} F _{2.9}	58.3	58,950	55,555	15

^a G' , storage modulus at 333 K under 1 rads^{-1} , ^b M_c , cross-linking mass determined as previously precised (paragraph 2–6). M_n , number average molecular weight of copolymers (PCL_xF_y) determined from SEC analysis.



Scheme 3. (PCL_{51.9}F_{4.9})-bis-maleimide adduct structure (D: furan moiety, A: maleimide moiety, DA: Diels–Alder bond).

Solubility

To verify the cross-linking of adducts, solubility tests were performed at room temperature in solvent of the initial (PCL_xF_y) copolymers and the multimaleimides. The adduct resulting of the (PCL_{72.4}F_{2.4}) copolymer and BisM was the only one to dissolve almost completely (Table V). When the furan average functionality increases, the rate of solubility of adduct decreases with both linker-agents. In the best case, 75–80% of the adduct mass became a polymer gel with BisM and TrisM, respectively.

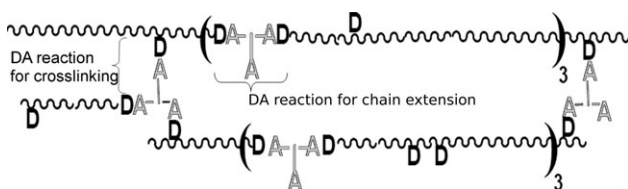
Thermoresponsive Behavior

Other solubility tests were performed at temperatures above 80°C on two samples of PCL_xF_y/TrisM adducts with a functionality of 2.4 and 4.9. If the cross-linking of the copolymer was due to the occurrence of DA reaction, the polymer gel could be converted by retro-DA reaction to a clear and fluid solution under heating. Figure 5 shows the comparative dissolution of two different adducts. After one hour at 90°C, the (PCL_{72.4}F_{2.4})/Tris-maleimide adduct with the lower furan functionality was totally dissolved [Figure 5(b)] while after 2 h at 90°C, the other adduct with the higher furan functionality is partially soluble [Figure 5(d)]. For this latter gel, the sample must be subjected to 120°C to disappear completely [Figure 5(e)]. Through the retro-DA reaction, the cross-linked copolycaprolactone in gel was converted back to the original (PCL_xF_y) and Tris-maleimide. From these results, it is concluded that our polycaprolactone gels have thermoresponsive behavior. What's more, the thermal response of the gels (temperature and time) can be adjustable with the furan amount *Y* of PCL_xF_y/Maleimide adducts.

Thermomechanical Properties

The viscoelastic properties of the (PCL_xF_y)/BisM and (PCL_xF_y)/TrisM adducts were analyzed using oscillatory thermal tests to verify their thermoresponsive properties and especially their thermoreversibility via DA and rDA reactions.

Frequency Sweep at 60°C (DA Coupling). Frequency sweep experiments performed at 60°C, 10–15°C above the melting temperature, are shown in Figures 6 and 7. For four studied



Scheme 4. (PCL_{51.9}F_{4.9})-Tris-maleimide adduct structure (D: furan moiety, A: maleimide moiety, DA: Diels–Alder bond).

specimens, a G' plateau was obtained especially in the low frequency region. The presence of these plateaus can unambiguously prove the formation of cross-linked adducts for PCL-diene having functionalities between 2.9 and 4.9. These experiments have not been conducted on the (PCL_{72.4}F_{2.4})/BisM adduct and the initial copolymers (PCL_xF_y) because G' values were too low to be measured in our conditions. Thus, the cross-linking nodes can only be assigned to DA chemical bonds between maleimide moieties of coupling agent and furan moieties of copolymers.

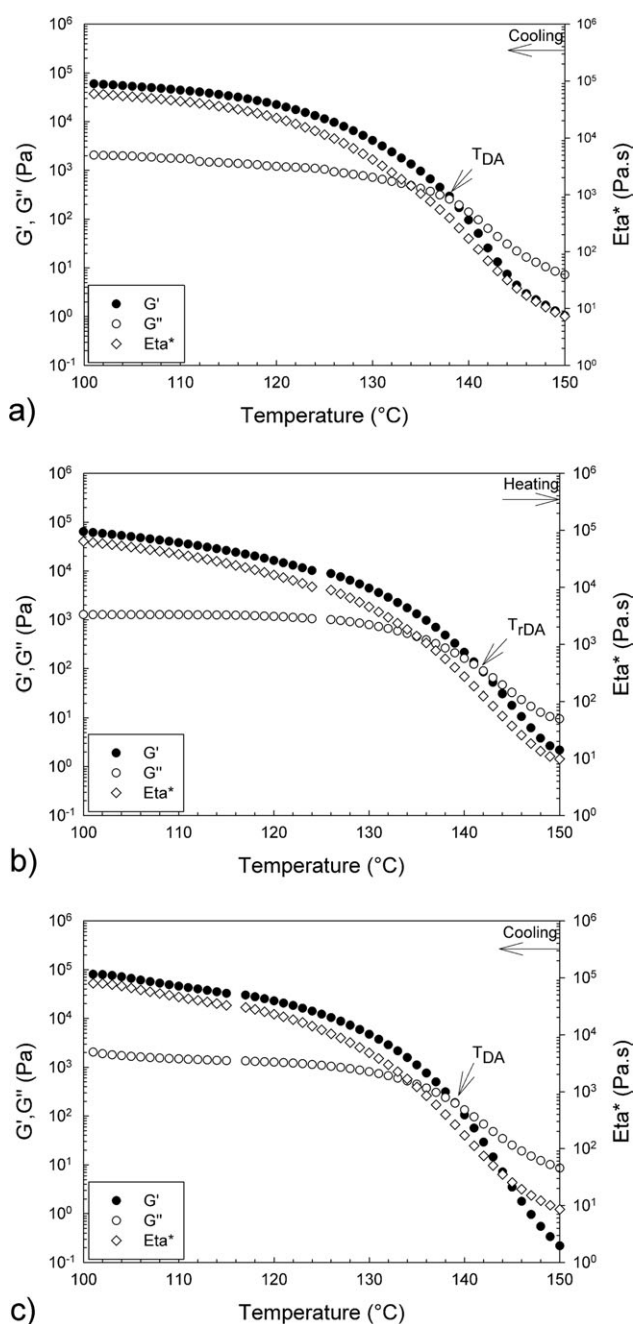


Figure 8. G' and G'' vs. temperature (1 rads^{-1}) for PCL_{51.9}F_{4.9}/Bis-maleimide. (a) cooling on the 1st cycle, (b) heating on the 1st cycle, (c) cooling on the 2nd cycle.

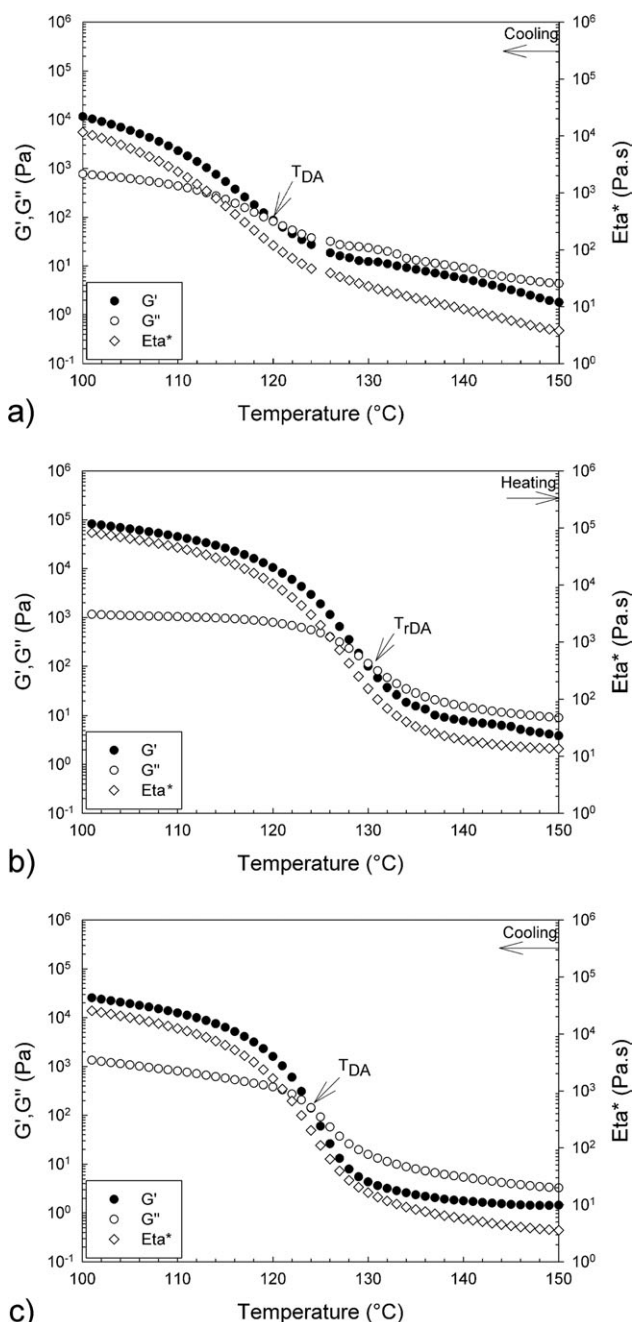


Figure 9. G' and G'' vs. temperature (1 rad s^{-1}) for $\text{PCL}_{51.9}\text{F}_{4.9}$ /Tris-maleimide (a) cooling on the 1st cycle, (b) heating on the 1st cycle, (c) cooling on the 2nd cycle.

The $(\text{PCL}_{72.4}\text{F}_{2.4})$ /Bis-maleimide adduct was probably not cross-linked because the conversion of DA reaction was not sufficient. According to the Macosko-Miller equation, the expected gel-point conversion via DA reaction (X_{DA}) (Tables VI and VII) is 89% and 68% for a $(\text{PCL}_{72.4}\text{F}_{2.4})$ /Bis-maleimide adduct gel and for a $(\text{PCL}_{72.4}\text{F}_{2.4})$ /Tris-maleimide adduct gel respectively and if stoichiometric conditions are taken into account. For all the other adducts, the expected X_{DA} values were far lower. Overall, G' plateau values increase with maleimide and furan functionalities of networks. However, some plateau values of the systems

Table VIII. DA and rDA Temperature Obtained by DMA Analysis of Adducts with Bis-maleimide at 1 rad s^{-1} , Cooling and Heating Rate = 1°C min^{-1}

PCL_xF_y	$T_{\text{DA}} (^\circ\text{C})$ 1 st cycle	$T_{\text{rDA}} (^\circ\text{C})$ 1 st cycle	$T_{\text{DA}} (^\circ\text{C})$ 2 nd cycle
$\text{PCL}_{72.4}\text{F}_{2.4}$	-	-	-
$\text{PCL}_{62.3}\text{F}_{3.8}$	109	124	115
$\text{PCL}_{51.9}\text{F}_{4.9}$	136	142	138
$\text{PCL}_{28.6}\text{F}_{2.9}$	125	138	-

based on Tris-maleimide are lower than with Bis-maleimide. These counterintuitive results are attributed to the DA reaction kinetic. The conversion rate can increase, especially for systems based on Tris-maleimide, by leaving samples for several hours at temperature above the T_{cryst} . Tests were performed on several samples stored during 12 h at 60°C and have shown that, as expected, all G' plateau rose up.

The M_c values determined from G' plateau show that the DA reaction also takes part in copolymer chain extension. The ratio M_w/M_n allows an estimate of the chains' number between entanglements. The structures of adducts based on $(\text{PCL}_{51.9}\text{F}_{4.9})$ can be represented by Schemes 3 and 4.

Temperature Sweep at Constant Frequency. The DMA analysis for (PCL_xF_y) /Bis-maleimide and Tris-maleimide adducts were performed at a constant frequency in the temperature range of $150\text{--}60^\circ\text{C}$ on the sample cooling and then from 60 to 150°C on the sample heating. The experiments were started at a high temperature to give maximum chain mobility. The sample was then subjected to a slow cooling to promote the reaction of DA. Under these experimental conditions, the cross-linking begins and tends towards equilibrium well above the crystallization temperature. Figures 8(a,b) and 9(a,b) show the results obtained with the $\text{PCL}_{51.9}\text{F}_{4.9}$ /Bis-maleimide and $\text{PCL}_{51.9}\text{F}_{4.9}$ /Tris-maleimide adducts, respectively. They highlight a crossing of the G' and G'' vs. temperature curves located at 136 and 120°C on cooling and at 142 and 130°C on heating. This G'/G'' curves crossing was observed in all adduct samples between 88 and 136°C on cooling and between 113 and 142°C on heating. This curve crossing was named T_{DA} on cooling because below this, the DA reaction is favored compared to rDA reaction. By contrast, on heating, the rDA reaction becoming predominant above the gel-temperature, this point was noted T_{rDA} , (Tables

Table IX. DA and rDA Temperature Obtained by DMA Analysis of Adducts with Tris-maleimide at 1 rad s^{-1} , Cooling and Heating Rate = 1°C min^{-1}

PCL_xF_y	$T_{\text{DA}} (^\circ\text{C})$ 1st cycle	$T_{\text{rDA}} (^\circ\text{C})$ 1st cycle	$T_{\text{DA}} (^\circ\text{C})$ 2nd cycle
$\text{PCL}_{72.4}\text{F}_{2.4}$	88	113	86
$\text{PCL}_{62.3}\text{F}_{3.8}$	105	118	109
$\text{PCL}_{51.9}\text{F}_{4.9}$	120	130	124
$\text{PCL}_{28.6}\text{F}_{2.9}$	122	131	127

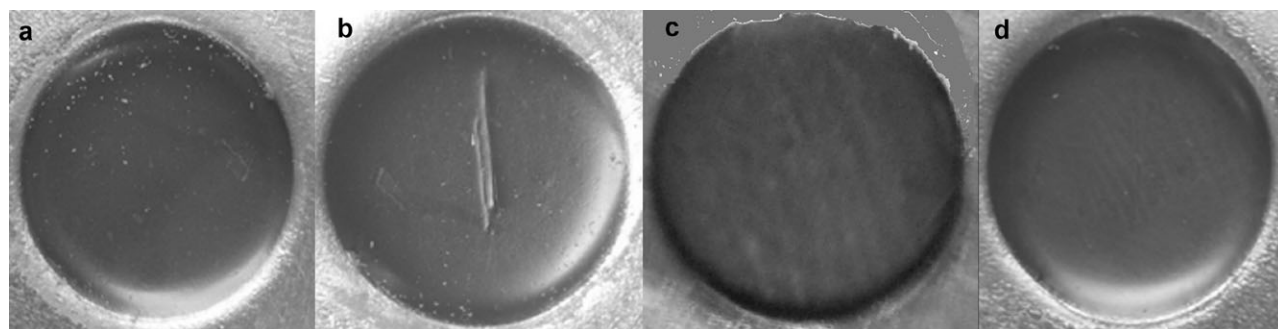


Figure 10. Test of remendability of (PCL_{51.9}F_{4.9})/Tris-maleimide adduct. (a) Initial crosslinked adduct, (b) knife-cutting sample, (c) Thermally treatment sample, (d) Repaired sample.

VIII and IX). About these points, the observed variations of the values G' and G'' are in the range of 10^5 – 10^0 and 10^4 – 10^1 , respectively. At elevated temperatures, adducts exist as liquids with the values of loss modulus (G'') higher than storage modulus (G') and inversely at temperatures lower than T_{rDA} . For two series of adducts, the temperature ranges in which the DA reaction is predominant against the retro-DA reaction increase with the (PCL_xF_y) copolymers' size decreasing and the cross-linking density increasing. In others words, the network may be broken more easily when the diene functions belong to a looser network.

A second cycle of temperature sweep was conducted. As observed in Figures 8(c) and 9(c), the repeatability of results and finally, the thermoreversibility of networks were verified.

Although these results should strongly depend on the rate at which the temperature is changed at constant frequency, this DMA analysis is of a particular interest for semicrystalline polymeric networks because it can determine quickly and exactly the two predominant domains of the DA and rDA reactions that are located on both sides of gel temperature as well as the reprocessing domain.

Self-Healing Properties

On the PCL_{51.9}F_{4.9}/TrisM adduct, the self-healing property was also observed (Figure 10). In the initial conditions, the material was prepared so that its surface was flat and smooth [Figure 10 (a)]. A scratch was made on the sample's surface by knife-cutting [Figure 10(b)]. The cut sample was then thermally treated at 140°C for 20 min then at 40°C for 12 h. The debonding of the gel occurred at 140°C (rDA) leading to the fluidization of the material and to self-repair [Figure 10(c)], whereas the rebonding occurred at 40°C (DA) to reform the cross-linked structure. After this treatment, the scratch on the sample was repaired, as it can be seen in Figure 10(d). The crack-healing ability of the developed material was thus demonstrated.

CONCLUSIONS

A series of polydienes based on furan-containing polycaprolactones of average functionality between 2.4 and 4.9 was synthesized without solvent and carefully characterized. Two series of DA adducts from these polydienes and a Bis or Tris-maleimide compound were performed in the melt then cooled. Semicrystalline DA networks have been obtained with conversion rates

that can be as low as 40%. It was shown that the DA reaction contributes also to the chain extension and allows to obtain loose networks. Their thermal properties were determined and their thermal-responsive properties, thermal reversibility and self-healing ability were highlighted. The gel-temperatures of DA networks were clearly and repeatedly demonstrated by rheological analysis. The reprocessing temperature domain depends on the cross-linking density of DA networks.

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