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Synthesis and Thermomechanical Properties of Allyl-Functionalized Polycaprolactone Urethane-*co*-2-Hydroxylethyl methacrylate Networks

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ABSTRACT: PCL-segmented multiallyl-functionalized poly (ester urethane) prepolymers (PEUs) were prepared in a two-step process. First, hydroxyl-terminated PCL and glycerol simultaneously reacted with an excess of a diisocyanate, the obtained isocyanate functionalized prepolymers then reacts with allyl amine. PEUs structure choice mainly focused on two aspects: the PCL segments concentration and the allyl functionality that, respectively, affects the biodegradability and the density of the issued networks. The concentrations of the different reactants were fixed, taking into account the desired mean structure and also to prevent crosslinking during the synthesis of the prepolymers. FTIR was principally used to monitor the synthesis of allyl functionalized PEUs. The carbonyl absorption of PCL, initially located at 1720 cm^{-1}, reaction of the PCL and shifted toward 1730 cm^{-1}, due to a decrease in crystallinity as confirmed by DSC. The structure of allyl-functionalized PCL-segmented PEU analyzed by ^{1}H NMR, double bond content was between 0.2 and 1.2 mmol g^{-1}. Networks were obtained by UV-initiated radical copolymerization of allyl-functionalized PEUs and HEMA. The effects of PCL concentration and molar mass on their thermomechanical and thermal properties were analyzed. Particular damping properties were obtained. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41295.

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INTRODUCTION

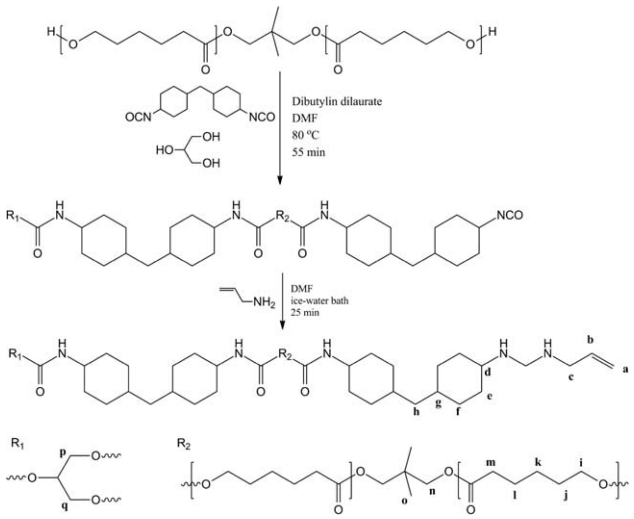
Poly ester urethanes (PEUs) are particularly versatile polymers that can be used as coating material, optical fiber coating, or in preparing high-strength composites[1–3] and scaffolds in tissue engineering.[4,5] When double-bond functionalized, these PEUs can be crosslinked or co-crosslinked when copolymerized by chain addition with other unsaturated monomers,[6,7,12] this leads to substantial evolutions of the thermomechanical properties of issued materials. Recently, a particular interest is given again to Poly(ε-caprolactone) (PCL), a biodegradable polymer having potential applications in biomedical fields.[8–11,20] For these reasons, this study focuses first on the synthesis of multibranched PEUs bearing PCL segments and double-bonds end functions.

Polyurethanes are usually synthesized in two steps[12,13]: First, a telechelic dialcohol reacts with a diisocyanate (with molar ratio of alcohol to isocyanate equals with 2) to obtain linear telechelic dialcohol. Then, hydroxyl end groups of these prepolymers react with acyl chloride (such as methacryloyl chloride), leading to double-bonds end functions. This two-step process is very efficient and generally leads to well-defined and controlled double-bound functionalized prepolymer. However, the functionality is limited and the double-bond concentration is low. Furthermore, this process is difficult to be scaled up in industrial production.

So, a new, facile and effective method in which the above mentioned disadvantages are avoided is proposed in this study. This method yields original branched prepolymers having variables double-bond functionalities and relatively high double-bonds concentrations.

First, several multialcohols are used simultaneously with isocyanate excess, giving multiisocyanate terminated prepolymers. Then these pre-polymers react with ally amine, leading to allyl-functionalized PEUs.

These PEUs were copolymerized with 2-hydroxyethylmethacrylate (HEMA). The effect of the PEUs structure on the viscoelastic and



Scheme 1. The 2-step synthesis of allyl-functionalized and PCL-segmented PEUs labeled for ^{1}H NMR.

thermal properties of the issued networks were studied. The thermal properties of the obtained networks were analyzed to determine their upper service temperature, their properties at thermal environment in addition to their toxicity at high temperature.

EXPERIMENTAL

Materials

Dihydroxyl-terminated polycaprolactone oligomers CAPA^{TM} 2100A, 2200A, and 2402 were purchased from Solvay. Their M_n are 1000, 2000, and 4000 Da, respectively, as indicated by the supplier and confirmed by ^{1}H NMR. 2-Hydroxyethyl methacrylate was purchased from Röhm GmbH. 4, 4′-Methylenebis (cyclohexyl isocyanate) (H_{12}MDI), Glycerol, 1, 4-butanediol, Dibutyltin dilaurate, Allylamine, Tin(II)-bis-(2-ethylhexanoate) were purchased from SIGMA-ALDRICH (France). Anhydrous DMF and diethyl ether were purchased from Carlo Erba Reagents^{TM}. The photo initiator was composed as follows: 60 wt % of CN381 from Sartomer (containing copolymerisable amine acrylate as synergist), 20 wt % of Benzophenone (99%) from Aldrich, and 20 wt % of 2, 2-Diethoxyacetophenone from Aldrich. The 2-Hydroxyethyl methacrylate was distilled before use; glycerol was dehydrated by molecular sieves 3 Å (rod shape, size 1/16 inch, Fluka) for 1 week before use. All other reagents were used as received without further purification.

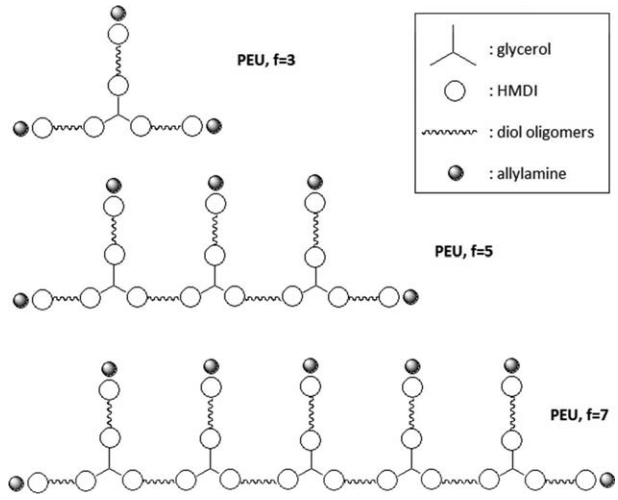


Figure 1. Expected structures of the PCL-segmented allyl-functionalized PEUs.

Synthesis

Synthesis of PCL-Segmented Prepolymer. Glycerol and the hydroxyl-terminated PCL oligomer were first introduced into a 2-neck flask equipped with dried nitrogen flow and condenser. Then anhydrous DMF was injected in as the solvent and the reactive system was magnetically stirred at room temperature. Then, the H_{12}MDI was injected in and mixed until the whole system becomes homogeneous. Finally, the dibutyltin dilaurate was introduced as catalyst and the system was placed in an oil bath at 80°C for 55 minutes. During the reaction, the FTIR was used to monitor the consumption of isocyanate group.

End-Capping of the PEUs Using Bifunctional Monomers. The obtained PEU solution above was diluted with anhydrous DMF and placed in the ice-water bath with magnetic stirring. Then allylamine was added drop wise to react with the remaining isocyanate groups. The reaction monitored by FTIR was kept for 30 min until the total consumption of isocyanate groups. Then the product was precipitated in a large amount of ethyl ether, the precipitator was three times redissolved in chloroform and reprecipitated in ethyl ether. Then, the product was collected and dried under vacuum at room temperature for 24 h and stored at −20°C.

Network Films Preparation by UV Curing. Allyl-functionalized PEU's were dissolved in HEMA with mass ratio M_{HEMA} : $M_{PEU} = 1.5 : 1$ at room temperature. The photo initiator was then added. Mixtures were placed in an ultrasonic oscillator to remove the air bubbles before curing.

For UV curing, the mixtures were transferred to LDPE molds ($100 \times 10 \times 100\ \mu$ mm^3) and cured in air by a fluorescent lamp, JAD STS-350, equipped with 8W × 3 fluorescent tubes offering $\lambda = 250$ nm UV light. The mixtures were exposed 3 cm from the lamps for 24 h.

Instrumentation

IR. FTIR was used to monitor the reaction of isocyanate groups with absorption at 2260 cm^{-1}, and quantitatively characterize the PEUs. The absorption spectra of the polymer were recorded on a Nicolet Nexus spectrometer (700–3500 cm^{-1}) using attenuated total reflectance (ATR) technique.

NMR Analysis. NMR analyses were performed with a Bruker Avance II spectrometer operating at 250 MHz for ^{1}H NMR. The analyses were performed with 5 mm diameter tubes containing about 25 mg of polymer in 0.5 mL chloroform-D, with tetramethylsilane as the internal reference at 0 ppm. All samples were scanned for 64 times at 300 K.

DSC. Differential scanning calorimetry (DSC) measurements for the allyl-functionalized PCL-segmented PEUs and PEU/pHEMA networks were carried out with a Q10 calorimeter from TA Instruments. Samples were transferred to hermetic

Table I. Formulae Design of the Allyl-Functionalized PCL-Segmented Polyurethanes

Entry	Expected allyl functionality	PCL segment number in the expected structures	M_n of the used PCL (Da)	Mole ratio of the reagents (H_{12}MDI : glycerol : PCL : allylamine)
Run 1	3	1	1000	4.41 : 1 : 1 : 3
Run 2	3	2	1000	5.52 : 1 : 2 : 3
Run 3	3	3	1000	6.62 : 1 : 3 : 3
Run 4	3	3	2000	6.62 : 1 : 3 : 3
Run 5	3	3	4000	6.62 : 1 : 3 : 3
Run 6	5	5	1000	15.43 : 1 : 5 : 5
Run 7	5	7	1000	17.65 : 3 : 7 : 5
Run8	7	7	1000	31.97 : 5 : 7 : 7
Run9	7	11	1000	28.7 : 5 : 11 : 7

pans and sealed, then analyzed from −80°C to 210°C with a cooling/heating rate of 10°C min^{-1}. The glass transition temperatures were evaluated from the data recorded during heating by identifying the inflection points. Each sample underwent two cycles of heating–cooling cycles.

SEC. For the analyses of allyl-functionalized PCL-segmented PEUs, size exclusion chromatography (SEC) was conducted using a system equipped with refractive index (Waters 2414) and light scattering (Wyatt MiniDawn Treos) detectors. Two columns HR1 and HR3 from Waters were used. The eluent was tetrahydrofuran (THF) with a flow rate of 1 mL min^{-1} and the elution temperature was 35°C. The copolymers' molecular weights were determined using a calibration curve established on a set of narrow polystyrene standards of different molecular weights ranging from 500 to 700,000.

Dynamic Mechanic Analysis. The dynamic mechanical thermal analyses of the PEU/pHEMA network films were performed with Rheometrics Solids Analyzer (RSA II, TA-Instruments) to obtain tensile dynamic mechanical spectra. Test samples were cut from the previously cured strips with a predetermined shape (40 mm × 10 mm × 100 μm). For dynamic tensile measurements, a nominal strain of 0.1% was adapted, with an applied frequency of 1 Hz. Storage modulus E', loss modulus E'', and loss factor tan δ were determined as a function of temperature. Data were taken from −90°C to 150°C using a heating rate of 3 °C min^{-1}. Each sample was equilibrated in the same chamber under dry nitrogen at the starting temperature before running the test.

Thermogravimetric Analysis (TGA). A thermogravimetric analyzer (TGA) from Mettler Toledo, TGA/DSC 1, was used. Thermal degradation experiments were done under nitrogen purge with a flow rate of 80 mL min^{-1} for all experiments. Samples ranging from 15 to 20 mg were heated from ambient temperature to 550°C with a heating rate of 10°C min^{-1}.

For the TGA–FTIR study, the TGA was interfaced with a Thermoscientific Nicolet™ Fourier transform infrared (FTIR) spectrometer using TGA/FTIR interface. The IR cell and the heated line transferring evolved gases from the TGA to the FTIR were

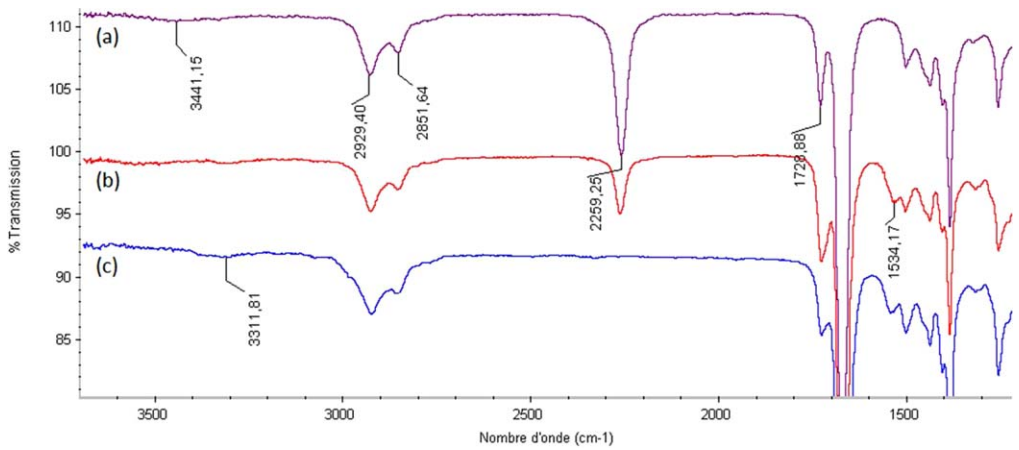


Figure 2. FTIR spectra monitoring PEU Run3 syntheses (a) reactants at initial time, (b) prepolymer after the first step of synthesis, (c) after the second step. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

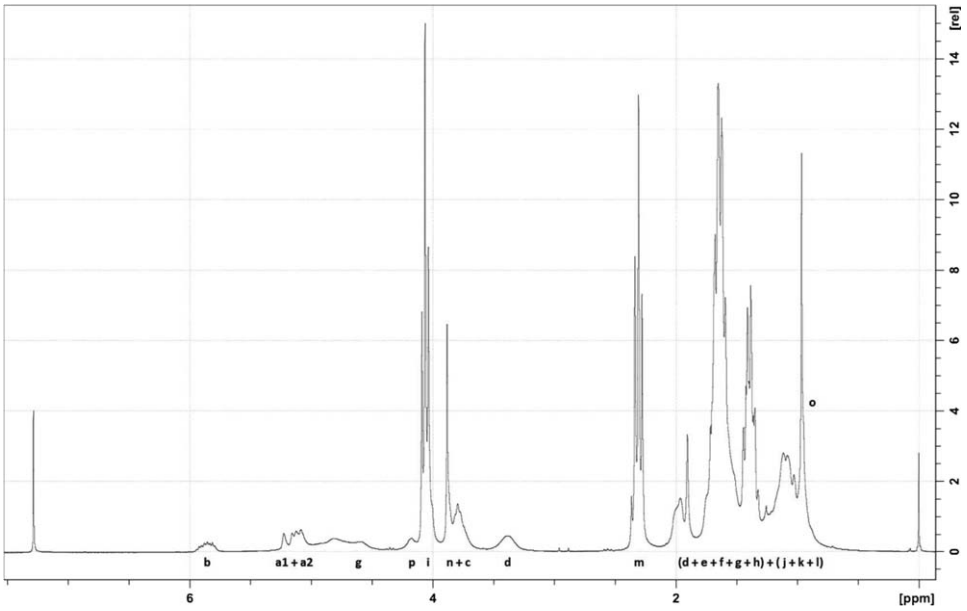


Figure 3. ^{1}H NMR spectra of a polyurethane sample (Run3) in Chloroform-D at 298 K.

maintained at 225°C and 215°C, respectively. IR spectra were recorded in the spectral range of 4000–500 cm^{-1} with a 4 cm^{-1} resolution throughout the degradation analyses.

RESULTS AND DISCUSSION

Syntheses and Characterizations of PCL-Segmented Multiallyl-Functionalized Poly(ester urethane) prepolymers

PCL-segmented multiallyl-functionalized pre-polymers were prepared in a two-step process: first hydroxyl-terminated PCL and glycerol simultaneously reacted with an excess of H_{12}MDI, the obtained isocyanate functionalized prepolymers then react with allyl amine.

An example is given in scheme 1

Structure Design of the Poly(ester urethane)s

PEUs structure choice mainly focused on two aspects: the PCL segments concentration and the allyl functionality that affects the biodegradability and the density of the issued networks.

To endow the PEU with different functionalities, different structures were designed as illustrated in Figure 1. Actually, these perfect structures are neither expected nor obtained because the different alcohols present in the reactive system randomly reacts with the diisocyanate and leads to different structures. Figure 1 only presents the average structures. Nevertheless, the functionality and chain end concentration are realistic.

The concentrations of the different reactants were fixed, taking into account the desired mean structure and also to prevent cross-linking during the synthesis of the prepolymers. For doing so, eqs. (1)–(3) of Macosko-Miller[14] were used to prevent cross-linking during the PEU's synthesis, the calculated gel conversion, p_{gel}, must be above 1.

$$P_{gel}^{2} = \frac{1}{(\bar{f}_a - 1)(\bar{f}_b - 1)} \times \frac{1}{r} \quad (1)$$

$$f_i = \frac{\sum n_i f_i^2}{\sum n_i f_i} \quad (2)$$

$$r = \frac{n_{Af_A}}{n_B f_B} \quad (3)$$

For eqs. (1)–(3), A and B are respectively hydroxyl and isocyanate groups, and r is the mole ratio of these two functions; f_i is the functionality of monomer i, $\bar{f}_i$ is the mean functionality of i. By calculating the content of each compound to achieve the expected structures, the designed formulae are listed in Table I.

Synthesis Monitored by FTIR

FTIR was principally used in this study to monitor the synthesis of allyl functionalized PEU (Figure 2). The absorption at

Table II. Chemical Shift of Protons from Allyl-Functionalized and PCL-Segmented PEUs

Proton	a1	a2	b	c	d	e1	e2	f1	f2	g
Chemical shift (ppm)	5.22	5.12	5.84	3.83	3.37	1.12	2.00	0.95	1.70	1.25
Proton	h	i	j	k	l	m	n	o	p	q
Chemical shift (ppm)	1.06	4.06	1.62	1.29	1.53	2.31	3.88	0.96	4.20	4.64

Notes: all protons were labeled in Scheme 1.

Table III. The Average Ratio of Repeat-Unit CL to Double-Bond Functions in Allyl-Functionalized PCL-Segmented PEU Moles, by Idea Value and by Real Value, Respectively

Sample names	Run3	Run7	Run9
Functionality of expected structured PEUs	3	5	7
Expected [double bond function]/[CL] repeat unit, mol : mol	1 : 8	1 : 11.2	1 : 12.6
Calculated [double bond function]/[CL] repeat unit by ^{1}H NMR results, mol : mol	1 : 8.4	1 : 10.9	1 : 14.2

2259 cm^{-1} (assigned to N=C=O) decreased gradually during 55 min and then became constant, indicating the total consumption of the alcohol groups and the end of the first step that leads to urethane functions. At the end of the second step (reaction of amine with isocyanate giving urea functions), the N=C=O absorption completely disappeared, confirming the total reaction of isocyanate with the amine groups of allylamine. The carbonyl absorption of PCL, initially located at 1720 cm^{-1}, Reaction of the PCL and shifted towards 1730 cm^{-1}, due to a decrease in crystallinity.[15] This evolution will be confirmed by DSC.

Allyl-Functionalized PEU Structure Evolution by ^{1}H NMR

The structure of allyl-functionalized PCL-segmented PEU illustrated above in Scheme 1 was analyzed by ^{1}H NMR, a spectrum is shown as example in Figure 3. The attributions of the protons labeled in Scheme 1 are in Table II.

As can be seen in Table II, several protons were overlapped at 0.9–2 ppm and 4–4.6 ppm. However, some characteristic protons from each part of the PEU can be clearly observed: Allyl protons a and b from allylamine were located at 5.8 ppm and 5.2 ppm; α and ε methylene protons (labeled with I and m) from PCL oligomer chains can be seen at 4.0 ppm and 2.2 ppm, respectively. Protons from the PCL co-initiator, 2, 2-dimethyl-1, 3-propanediol, were assigned as j and f.

The average mole ratio of CL repeat unit to allyl function can be calculated by comparing the integration of protons b (allyl proton of allylamine) and e (α methylene proton from CL). Results are depicted in Table III. These ratios are in concordance with those expected, confirming that the mean structure expected by modeling was obtained.

Table IV. Molar Mass and T_g of PCL-segmented Allyl-Functionalized PEUs Synthesized with Different Parameters

Entry	M_n/M_w/MWD	T_g of allyl-functionalized PEU prepolymers	Double bond content, mmol/g
Run1	6300/22400/3.56	−34.1	1.23
Run2	7200/17400/2.41	−34.4	0.80
Run3	9410/23200/2.47	−38.0	0.59
Run4	15700/31200/1.99	−56.2	0.37
Run5	30400/53700/1.77	−56.8	0.21
Run6	9100/26700/2.93	−34.3	0.55
Run7	11400/33100/2.90	−40.2	0.40
Run8	11230/28740/2.56	−36.2	0.62
Run9	15320/50280/3.32	−40.9	0.35

As a reminder, U-F3-A1-M1000 means allyl-functionalized PCL-segmented PEU with expected functionality 3 (F3), and average 1 PCL chains (A1) owning molar mass 1000 (M1000) in each PEU mole.

Allyl-Functionalized PEU Syntheses Evolution by SEC

To verify the correct evolution of the synthesis when changing the reaction parameters, SEC analyses were also performed. The results are summarized in Table IV.

The molar mass evolutions are coherent with the expected structures of the allyl-terminated PEUs. When comparing Run1, Run2, and Run3, the more PCL segments are introduced into the PEU, the larger molar mass of the PEU has, with sharper molar mass distribution (MWD), which is in accordance with the former reports.[16] An increase of the molar mass of the PCL segments from Run3 to Run5 will have the same effect in increasing the molar mass of these polyurethanes. When investigating the functionality effect on molar mass from Run3 and Run6-Run9, it can be seen that the molar mass of PEUs increased with the increase of their functionality; it is reasonable because the polyurethane having larger functionality or more PCL segments have higher molar mass, as illustrated in Figures 1 and 4.

Characterization of the PCL-Segment by DSC

DSC results are depicted in Table IV. According to these results, only one T_g attributed to PCL rich-phase was observed. All the prepared PEU's in this study have higher T_gs when comparing with the T_g of pure high molar mass PCL (−60°C), which confirms that these phases are not only composed of PCL but that they also contain PU segments. Only for run4 and 5 with PCL segment $M_n = 2000$ and 4000, T_gs of the polyurethanes approach that of PCL. This result was also expected, since for these runs the isocyanate segment content in PEU's is particularly low, consequently, their effect on the T_gs is also reduced. More information on the structure of these PEU's will be obtained in the next parts.

Crosslinking of pHEMA by Allyl-Functionalized PCL

The average functionality of this reactive system composed of allyl-functionalized PEUs and HEMA is higher than 2, consequently, crosslinking should occur. In this study, the PEUs have good solubility in HEMA for the selected mass ratio. Solutions of different PEUs in HEMA monomer were prepared, with also the introduction of the photo initiator, yielding transparent homogeneous solutions. After the UV-curing (copolymerization of the allyl functions of PEUs and the double bonds of HEMA), transparent and flexible films were obtained. As expected, these films are not soluble in solvents of the reagent mixture

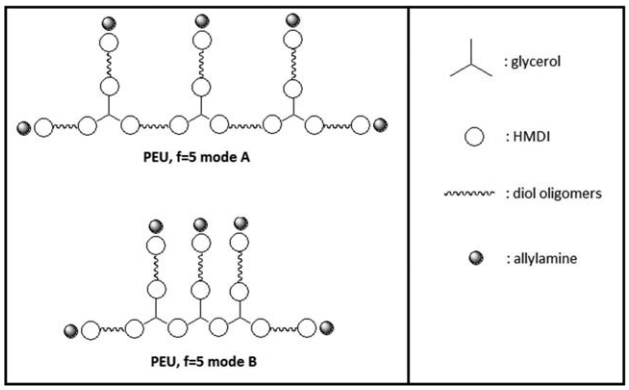


Figure 4. Expected structures of PCL-segmented allyl-functionalized PEU with functionalities equal to 5, corresponding to the Run6 and Run7 in Table III.

(e.g., THF and Chloroform). Thermomechanical properties of these films are analyzed in this part.

As shown in Figures 5–7, the storage moduli E′ are higher than loss moduli E″ throughout temperature ranges in all experiments. The rubbery plateaus are also obtained at high

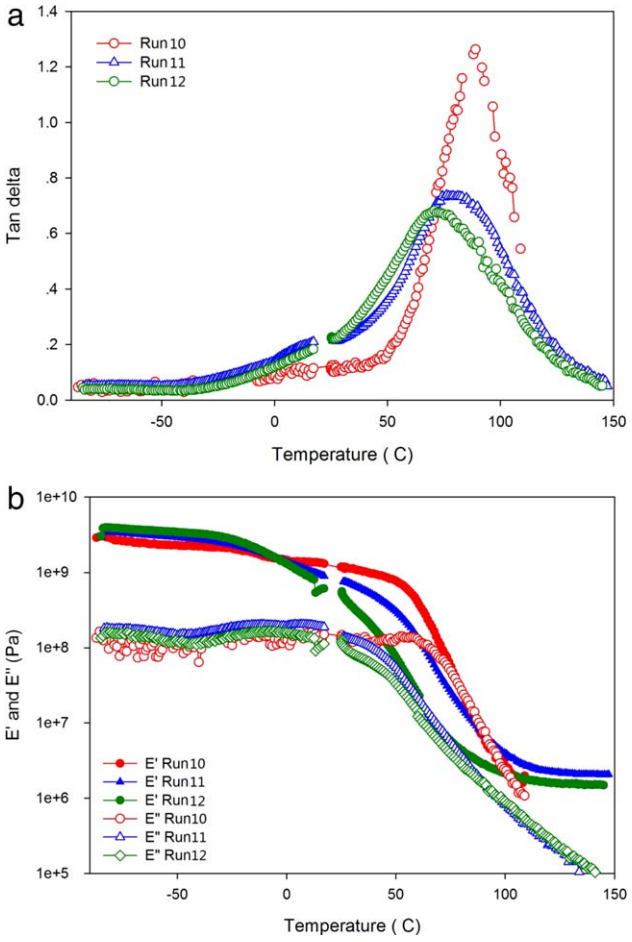


Figure 5. Storage modulus (E'), loss modulus (E") and loss factor tan δ versus temperature of the PEU/pHEMA networks 10, 11, and 12. [Color figure can be viewed in the online issue, which is available at wileyonline library.com.]

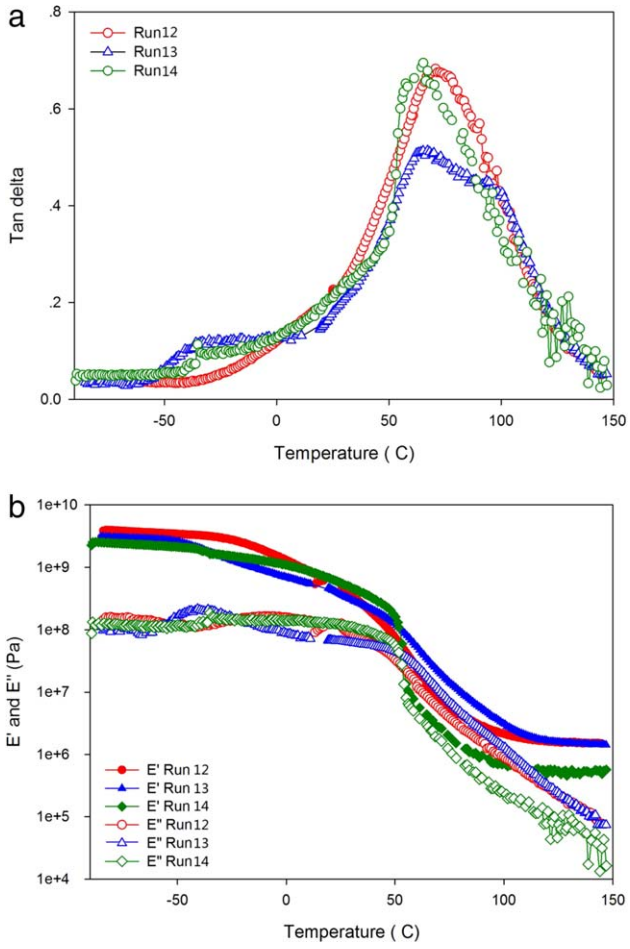


Figure 6. Storage moduli (E′), loss moduli (E″) and loss factor tan δ versus temperature curves of the PEU/ pHEMA networks based on PEUs Run3, Run4 and Run5 with different molar masses of PCL-dialcohol segments. The structures of PEUs were designed as in Figure 1, $f = 3$. [Color figure can be viewed in the online issue, which is available at wileyonline library.com.]

temperature. This confirms again the formation of the networks. Thermomechanical characteristics of these networks are summarized in Table V. The tan δ_{max}, working area of damping, and storage moduli of rubbery plateau were directly taken from Figure 5–7.

Effect of PCL Number on Triallyl-Functionalized PCL-Segmented PEU-Based Network

For Runs 1–3, Triallyl-functionalized PEUs contains 1, 2, and 3 PCL segments, respectively. By cross-linking HEMA with these PEUs, networks were obtained (runs 10–12). These networks contain, respectively, 14.4, 18.7, and 20.78 wt % of PCL. The DMA graphs are shown in Figure 5.

Noting the presence of two tan δ_{max} (one for PCL rich phase around 25°C and one for pHEMA rich phase around 90°C), increase of PCL mass fraction from 14 to 20 wt % and the two transitions become closer. This is particularly visible for tan δ_{max} pHEMA rich phase that shifted toward lower temperature from 89 to 64°C. This result confirms the

Table V. Thermomechanical Properties of the PEU/HEMA Networks

Entry	PEUs used in network syntheses	PCL content in the network, wt %	Maximum Tan δ (°C)	Tan δ_{max} value	Working area of damping (Tan δ > 0.3), (°C)	Storage moduli at rubbery plateau, (MPa)
Run10	Run1	14.4	88.9	1.26	58.8-122.3	/
Run11	Run2	18.7	76.1	0.74	43.2-114.6	2.07
Run12	Run3	20.7	70.8	0.68	37.8-108.5	1.51
Run13	Run4	25.5	65.2	0.51	43.8-111.0	1.45
Run14	Run5	29.0	65.3	0.69	43.9-103.0	0.54
Run15	Run7	20.8	82.9	0.96	52.3-116.1	1.50
Run16	Run9	20.9	82.8	1.10	53.4-118.7	0.79

compatibilization of the two phases. At the same time the working area of damping of the material becomes wider, as a result of an increase in intermediate structures where two phases are interconnected.

Effect of Oligomer Chain Molar Mass on Networks

The effects of the molar mass of the PCL segment (Run 10, 13, and 14) on the networks are illustrated in Figure 6.

A reduction in T_g is expected with the increase of the PCL content (from 14.4 to 25.5 and 29.0 wt %) and also with the increase of the mass between cross-links (M_c). Noting that the increase of M_c is due to the decrease of double bond functionality of the acrylated prepolymers (from 0.32 to 0.19 and 0.10 mmol g^{-1}), this decrease of T_g is compensated by the increase of the molar mass of the PCL (from 1000 to 2000 and 4000 Da), which increases the T_g of the network. As a result, there is almost no change in the glass transition of these networks.

Effect of PEU Functionality on Networks

Networks were prepared using PEUs with functionalities 3 (Run3), 5 (Run7), and 7 (Run9) in runs 12, 15, 16. Their thermomechanical properties are depicted in Figure 7.

Networks based on PEU $f = 7$ (Run9) and PEU $f = 5$ (Run7) seem similar since they contain the same PCL concentration with similar molar mass. In addition, they also have the same double bond concentration. As seen in Figure 7, the thermomechanical properties of these two specimens are almost equivalent with only a few differences: networks based on PEU $f = 7$ (Run9) have sharper tangent δ peak and lower rubbery plateau modulus when compared to networks based on $f = 5$ (Run7). For network based on PEU $f = 5$ (Run3), the PCL content is slightly lower than for $f = 7$ (Run9) and PEU $f = 5$ (Run7). The PEU from run 3 has similar soft / hard segment compositions as those from runs 7 and 9, but its double-bond concentration is obviously lower than for the other two specimens. This leads to a less dense network that has lower glass transition temperature. This network is more heterogeneous than the other two networks.

Thermogravimetric Analysis of the PEU/HEMA Films

The combination of thermogravimetric analysis and FTIR is a relevant technique for studying the decomposition of the products prepared here. The thermal degradation of the allyl-functionalized PCL-segmented PEU (from Run3) and that of the network prepared by its copolymerization with HEMA are given as examples. Figure 8 (a–c) depicts, respectively TGA, Differential TGA and Gram-Schmidt trace of the PEU and the issued network.

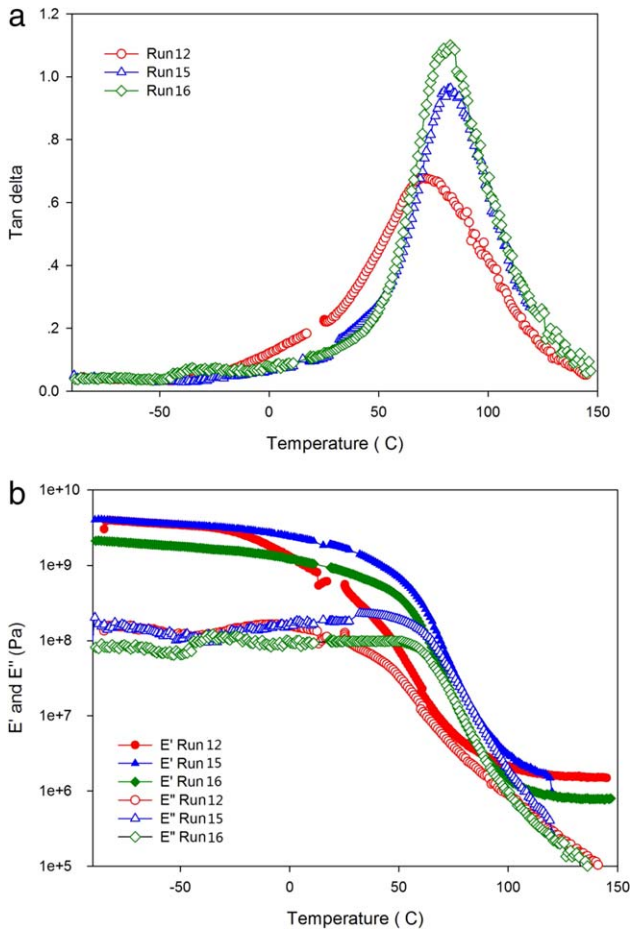


Figure 7. Storage moduli (E'), loss moduli (E'') and loss factor tan δ versus temperature curves of the tri-armed PEU/ pHEMA networks based on PEUs Run3, Run7, and Run9 possessing different functionalities. The structure of PEUs was designed using modes in Figure 1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

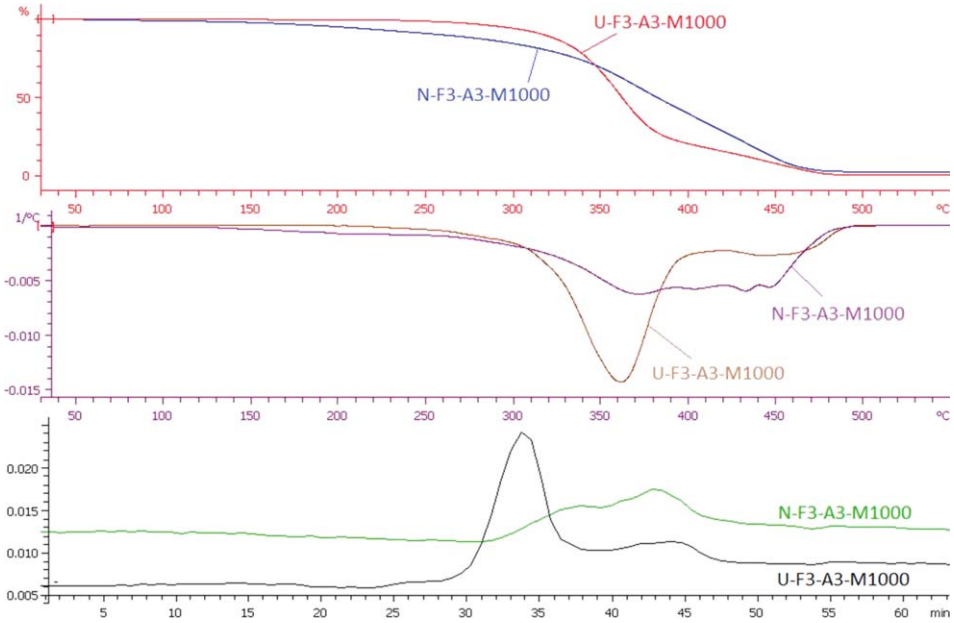


Figure 8. TGA (top), DTGA (middle) and Gram-Schmidt trace curves (bottom) of PEU Run3 and PEU/ pHEMA networks based on PEU Run3. The thermal degradations were conducted in nitrogen atmosphere from 30°C to 550°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For allyl-functionalized and PCL-segmented PEU Run3, its degradation steps were illustrated in Figures 8 and 9. The degradation begins with the decomposition of carbamate linkage to hydroxyl group and isocyanate, with the characteristic absorption of isocyanate group at 2259 cm^{-1} in spectra (A) of Figure 9 collected at 26.14 min (291°C), which corresponds with the decomposition of PU reported before.[17] However, this step cannot be seen in TGA and DTGA curves because the carbamate decomposition does not cause weight loss. Then, a major weight loss, with its maximum degradation rate around 362°C, was detected by TGA and DTGA curves. This weight loss is attributed to the degradation of PCL segments and confirmed by the IR spectrum of the gas generated at the same time. The main degradation product of PCL, 5-hexenioc acid, can be identified with its characteristic absorption at 2939 cm^{-1} $\gamma_{as}(CH_2)$, 2874 cm^{-1} $\gamma_s(CH_2)$, 1774 cm^{-1} $\gamma(C{=}O)$, 1642 cm^{-1} $\gamma(C{=}C)$, 1448 cm^{-1} $\delta(CH_2)$.[18]

Compared with the former report, degradation temperature of PCL segment in this PEU is lower, could be explained by the lower molar mass of the PCL oligomers. At the same time, strong signals of carbon dioxide at 2359 cm^{-1} and amine groups at 3340 cm^{-1} can be seen. These two peaks were believed to be the degradation products of isocyanate groups and H_{12}MDI fragment[19]and the allylamine fragment. From 430°C to 490°C, another obvious weight loss can be seen from TGA and DTGA curves. This is the further degradation of

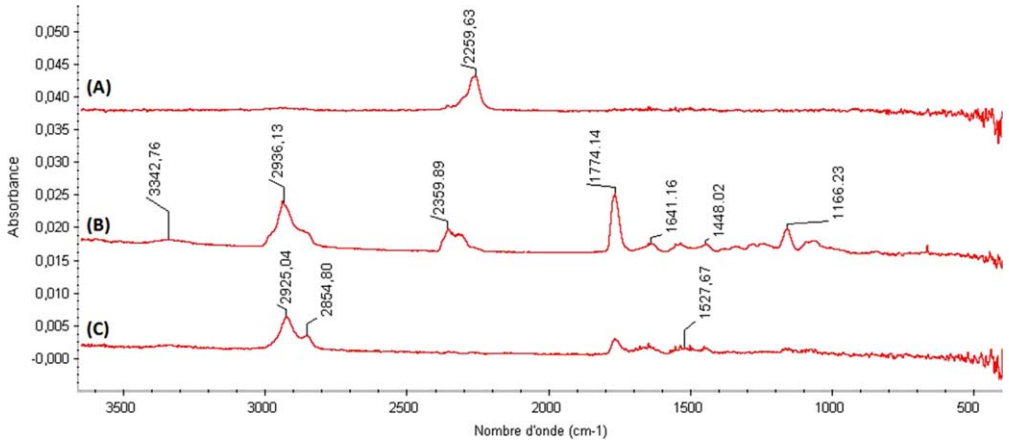


Figure 9. The FTIR spectra of gas collected during PEU Run3. The FTIR spectra was collected at the maximum evolution rate for each decomposition step for degradations at (A) 26.14 min (B) 33.70 min, and (C) 44.02 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

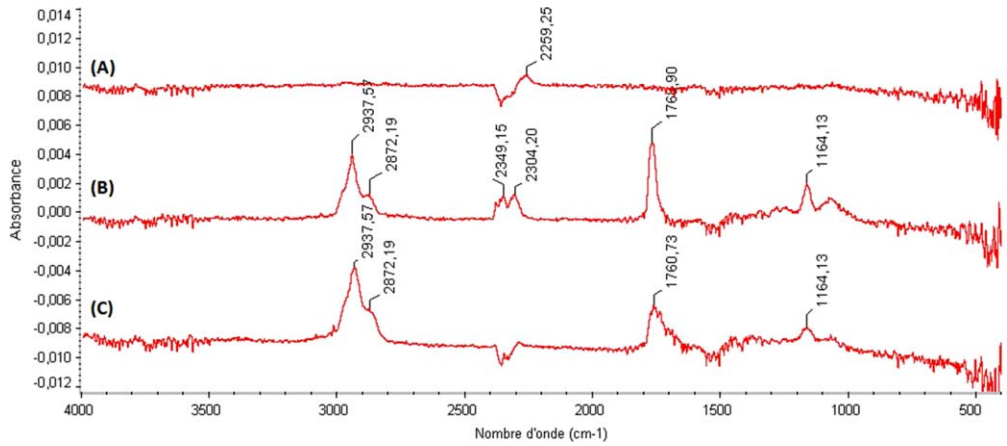


Figure 10. The FTIR spectra of gas collected during network Run12. The FTIR spectra were collected at the maximum evolution rate for each decomposition step for degradations at (A) 17.88 min (B) 35.76 min, and (C) 42.62 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

H_{12}MDI and corresponds to the degradation of H_{12}MDI segmented PU, reported by Cervantes with corresponding degradation temperature of H_{12}MDI.[19] Bands at 2931 and 2861 cm^{-1} were still observed and assigned to C-H absorptions. A broad band centered at 1520 cm^{-1} was also observed and was related to amine groups.[19] At the same temperature, this degradation is still accompanied by the degradation of remaining PCL segments until the end of the PEU degradation.

The IR spectra of the network Run12's degradation product in each degradation stage were shown in Figure 10. Compared with the allyl-functionalized PEU Run3, the network Run12 (based on Run3) is thermally stable below 130°C and has a flat gradient on weight loss during the thermal degradation with temperature ramping from room temperature to 550°C. Although the thermal degradation of network Run12 is more complex with its covalent bonded pHEMA chains, this network has similar degradation steps as its PEU composition Run3.

Compared with the PEU degradation TGA curves, the network starts to lose weight above 130°C, which is attributed to the depolymerization of pHEMA chains into HEMA according to the degradation of homo-polymerized HEMA reported before.[20] However, the HEMA absorption cannot be detected on the coupled IR. When continuously increasing the temperature, the characteristic isocyanate absorption at 2259 cm^{-1} was also found, which is the same as Run13, and corresponds to the decomposition of urethane links, followed by the degradation of PCL segments, with coupled IR absorption of 5-hexenioc acid shown in spectrum (B) in Figure 10. Furthermore, from the TGA and DTGA curves of the network, it can be seen that the maximum degradation speed of the PCL segments was delayed from 362°C to 370°C. This delay may be attributed to the restriction of the PCL segment's movement by covalent bond and hydrogen-bond interactions between carbamate group and hydroxyl group from pHEMA before degradation starts.

From 410°C to 490°C, the DTGA curve and especially the Gram-Schmidt trace of the network degradation are different from those of PEU. Obvious signals are detected around 410°C to 450°C in Gram-Schmidt trace, and their intensity is even stronger than the degradation of PCL segments, which can also be seen on DTGA curves. This weight loss is caused by the degradation of pHEMA chains, because the pHEMA segments have considerable content (60 wt %) in the network, and degradation temperature of homopolymerized HEMA reported by researchers[21] is similar to this temperature. When analyzing the gas from degradation of this stage, it can be seen that although the absorption of 5-hexenioc acid decreases, the 2931 and 2861 cm^{-1} band remain strong absorptions, as shown in spectrum (C) in Figure 10. These absorptions come from C-H absorptions of methylene and methine groups, coming from the fragment of the pHEMA chain products, which confirm again the depolymerization of pHEMA and the yield of the volatile HEMA monomer

CONCLUSIONS

Well-defined PCL based allyl-functionalized PEUs were synthesized. These PEUs were soluble in HEMA. UV curing of these transparent homogeneous solutions and consequently the copolymerization of PEUs allyl functions with HEMA yielded transparent and flexible films. The effect of the structure of the obtained networks on their dynamic mechanical properties was analyzed. Particular damping properties were obtained for some PEUs structures. Thermogravimetric analysis coupled with FTIR showed the degradation sequence and the degradation product of the PEUs and the issued network: For the PEUs, decomposition of urethane linkage occurred first, and was followed by the degradation of PCL segments reaching maximum degradation speed around 360°C. The degradation of H_{12}MDI fragment can be clearly seen in DTGA curves around 420–490°C. The networks shown similar degradation sequence with its PEU parts, but with higher depolymerization temperature of its pHEMA segments, around 440°C.

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