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Polymer 46 (2005) 11690–11697
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Synthesis and characterization of naphthoxazine functional poly(ε-caprolactone)

Baris Kiskan, Yusuf Yagci *

Chemistry Department, Faculty of Science and Letters, Istanbul Technical University, Maslak, TR-34469, Istanbul, Turkey

Received 20 June 2005; received in revised form 15 September 2005; accepted 15 September 2005
Available online 10 October 2005

Abstract

A novel naphthoxazine ring-containing poly(ε-caprolactone) (PCL) was synthesized and characterized. For this purpose, first hydroxyl functional naphthoxazine, namely 2-(1*H*-naphtho[1,2-e][1,3]oxazin-2-yl)-ethanol (N-a-OH) was prepared by the reaction of 2-naphthol, ethanolamine and paraformaldehyde either in bulk or in dioxane as solvent at 110 °C. Subsequently, N-a-OH was used as the coinitiator for the stannous-2-ethylhexanoate ($Sn(Oct)_2$) catalyzed living ring-opening polymerization of ε-caprolactone. The GPC, IR, ^1H NMR, UV, and fluorescence spectroscopic studies revealed that low-polydispersity PCL with naphthoxazine functionality at the end of the chain was obtained. The resulting PCL macromonomer undergoes thermal curing in the presence of low molar mass benzoxazine (P-a) at various temperatures with the formation of thermosets having PCL segments.

Keywords: Naphthoxazine; Polybenzoxazine; Poly(ε-caprolactone)

1. Introduction

Polybenzoxazines (PP-a) are class of phenolic polymers formed by thermal ring-opening of the corresponding benzoxazines (P-a). These polymers and their derivatives are of great interest for different scientific and industrial fields due to their superior mechanical and physical properties together with unusual thermal properties. Moreover, rich molecular design flexibility makes these polymers adequate candidates to function as high performance materials with a wide range of structural variations that should allow the properties of the cured material to be tailored for the specific requirements of individual applications.

P-a ring can also be opened at room temperature by cationic initiators [1] and the resulting polymers consisted of phenoxy type repeating units. More recently, we have shown that P-a can be polymerized by photopolymerization [2]. The structures of the polymers prepared by photoinitiated cationic polymerization were complex and related to the ring opening process of the protonated monomer either at the oxygen or nitrogen atoms.

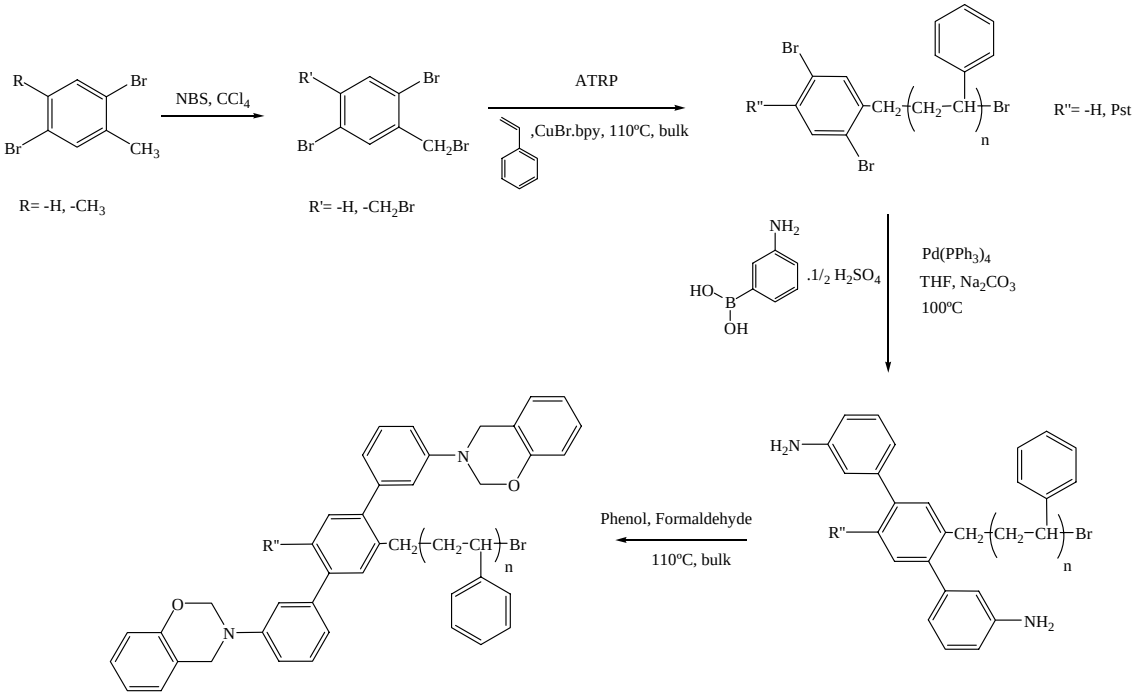
High performance properties of PP-a as thermosetting resins can further be improved by tightening their network structure. Moreover, additional properties for specific applications such as processabilty, flame retardancy and mechanical strength can be introduced by several ways. For example, thermal and mechanical properties of PP-a can be improved by blending with a polymer or clay. Maleimide based P-a polymers exhibit better thermal stability comparing with those of unmodified polymers and high char yield which gives good flame retardancy [3]. Similarly, chemical modification of novolac resins with benzoxazine rings or grafting of various phosphorous compounds to P-a modified resins forms nonflammable coatings [4,5]. It was also reported that P-a monomers with additional polymerizable acetylene functional groups form highly thermally stable cross-linked networks [6]. In another example *ortho*-, *meta*-, and *para*-phenylnitrile-functional P-a monomers are polymerized at different compositions with phthalonitrile-functional monomers yielding copolybenzoxazines of high thermal stability and easy processability [7].

We have recently proposed a macromonomer method for obtaining (PP-a)s with polystyrene segments. It was shown that P-a type macromonomers can easily be prepared from amino functional telechelics which were obtained via combination of ATRP and coupling processes [8]. The overall process is depicted below (Scheme 1).

It was reported that the miscible blends of polybisbenzoxazine (PB-a) and poly(ε-caprolactone) (PCL) can be prepared by an in situ curing reaction of benzoxazine in the presence of PCL. The miscibility was attributed to the intermolecular

* Corresponding author. Tel.: +90 212 285 3241; fax: +90 212 285 6386.
E-mail address: yusuf@itu.edu.tr (Y. Yagci).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.09.061



Scheme 1.

hydrogen bonding between the hydroxyl groups of PB-a and the carbonyl groups of PCL [9]. In a more recent work, Zheng et al. investigated the phase behavior and intermolecular specific interactions of the blends prepared in the same manner [10]. The detailed investigation with variable temperature FT-IR spectroscopy revealed that phenolic hydroxyl groups could not form efficient intermolecular hydrogen bonding interactions at elevated temperatures.

Herein, we report our approach to synthesize napthoxazine functional PCL macromonomers, upon curing in the presence of conventional benzoxazine monomer thermosettings of polybenzoxazines with covalently bonded PCL segments can be formed.

2. Experimental

2.1. Materials

Paraformaldehyde, ethanolamine, 2-naphthol, sodium sulfate (Na_2SO_4), aniline, sodium hydroxide (NaOH), acetic acid (Merck), diethyl ether, dichloromethane, (J.T. Baker), Stannous 2-ethyl-hexanoate (stannous octoate) (Sigma), 1,4-dioxane (Acros) were used as received. ε-Caprolactone (ε-CL) (Aldrich) was vacuum distilled over calcium hydride. Methanol was distilled before use. 3-Phenyl-3,4-dihydro-2*H*−1,3-benzoxazine (P-a) was synthesized according to literature [11].

2.2. General procedure for synthesis of 2-(1H-naphtho[1,2-e][1,3]oxazin-2-yl)-ethanol (N-a-OH)

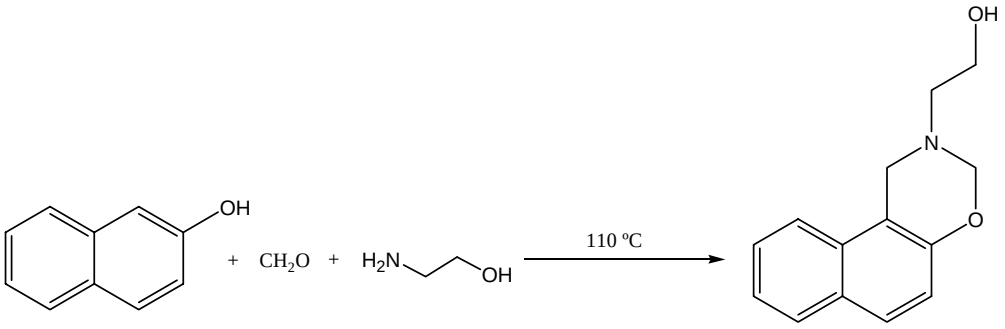
A 100 ml round-bottomed flask, equipped with magnetic stirrer and a reflux condenser, placed in ice bath, was charged with paraformaldehyde (0.03 mol) and ethanolamine (0.015 mol). 2-Naphthol (0.015 mol) was subsequently added to the mixture. The flask is then placed in an oil bath which is heated to 110 °C and the mixture was maintained at that temperature for 3 h. At the end of the reaction the mixture was diluted with dichloromethane and washed successively several times with 0.1 N NaOH and diluted AcOH solution. It was, then neutralized with distilled water. Organic layer was dried with anhydrous Na_2SO_4 and dichloromethane was evaporated to yield 2-(1H-naphtho [1,2-e][1,3]oxazin-2-yl)-ethanol (N-a-OH). Yield: 56%. The same synthetic procedure in dioxane as a solvent gave the same product with a relatively lower yield (49%).

^{1}H NMR ($CDCl_3$): $\delta = 2.57$ (broad s, 1H, OH), 3.00 (t, 2H, CH_2), 3.73 (t, 2H, CH_2), 4.34 (s, 2H, CH_2), 4.94 (s, 2H, CH_2), 7.00–7.04 (d, 1H, aromatic-3-position), 7.32–7.39 (t, 1H, aromatic-7-position), 7.45–7.51 (t, 1H, aromatic-6-position), 7.58–7.61 (d, 1H, aromatic-5-position), 7.63–7.67 (d, 1H, aromatic-4-position), 7.75 (d, 1H, aromatic-8-position).

IR (neat): 3370 cm^{-1} (O–H stretch), 3059 cm^{-1} (aromatic C–H stretch), 1750–1909 cm^{-1} (aromatic overtones), 1224 cm^{-1} (aromatic C–O stretch), 1072, 1038 cm^{-1} (C–O stretch), 940 cm^{-1} (aromatic ring mode) Anal. ($C_{14}H_{15}NO_2$) Calc. C, 73.34; H, 6.59, N, 6.11 Found C, 72.16; H, 6.22, N, 6.63.

2.3. General method for preparation of poly(ε-caprolactone) with the 2-(1H-naphtho[1,2-e][1,3]oxazin-2-yl)-ethoxy end group (PCL-N-a)

N-a-OH (0.001 mol), monomer (ε-CL) (0.02 mol) and stannous octoate (2.5×10^{-6} mol), were added under nitrogen in previously flamed and nitrogen-purged schlenk tube



Scheme 2.

equipped with magnetic stirrer. The ε-CL polymerization was carried out in bulk at 110 °C. After 48 h, the polymerization was terminated by cooling the tube to the room temperature, then diluted with CH_2Cl_2 and poured into 10-fold excess of cold methanol. The polymer with naphthoxazine end group was collected after filtration and drying at room temperature in a vacuum for 2 days. Yield: % 96.

2.4. Characterization

^{1}H NMR spectra were recorded in $CDCl_3$ with $Si(CH_3)_4$ as internal standard, using a Bruker AC250 (250.133 MHz) instrument. FT-IR spectra were recorded on a Perkin–Elmer FT-IR Spectrum One spectrometer. UV spectra were recorded on a Shimadzu UV-1601 spectrometer. Fluorescence spectra were obtained on a Perkin Elmer LS 50 Luminescence spectrometer. Differential Scanning Calorimetry (DSC) was performed on Perkin–Elmer DSC6 with a heating rate of 10 °C/min. under nitrogen flow. Molecular weights were determined by gel-permeation chromatography (GPC) instrument equipped with Waters styagel column (HR series2, 3, 5E) with THF as the eluent at a flow rate of 0.3 ml/min, Waters 410 differential refractometer detector and Waters 996 photodiode array detector. Number average molecular weight (M_n) values from ^{1}H NMR spectrum of the polymer were calculated by comparing the integral area of oxazine CH_2 at 4.92 ppm with that of the protons belonging to caprolacton units at 4.64–1.30 ppm.

3. Results and discussions

Tin octoate, $Sn(O(O)CCH(C_2H_5)C_4H_9)_2$, in short $Sn(Oct)_2$, is the most widely used [12] initiator to synthesize designed polymers based on PCL. In particular when used in conjunction with hydroxyl functional compounds or prepolymers, telechelics, linear and star-shaped block copolymers or networks can be obtained [13–21] via corresponding alkyl octoate formation. We have previously reported synthesis of novel end- and mid-chain functional macrophotoinitiators [22] and cyclohexene oxide macromonomers [23] of PCL by using appropriate hydroxyl group containing initiators. In view of the reported role of hydroxyl groups as initiators of the ring-opening polymerization, the 2-(1H-naphtho[1,2-e][1,3]oxazin-2-yl)-ethanol (N-a-OH) is expected to produce polymers containing a naphthoxazine group on one end of the chain.

It is well known that benzoxazine or naphthoxazine monomers can easily be prepared from primary amines, and phenols or naphthols with formaldehyde [24]. The synthesis of the initiator is shown in Scheme 2. In this connection it should be pointed out that benzoxazine type initiators can also be synthesized by following the same strategy. However, attempts to synthesize the corresponding initiator resulted in the formation of side products. Thus, the initiator was obtained only with a very low yield. Moreover, as it will be shown below, photochromophoric naphthalene ring present in N-a moiety gives possibility for the structural characterization of the intermediates at the various stages by using spectroscopic methods.

The structure of the initiator was confirmed by elemental analysis as well as spectroscopic investigations. The IR spectrum contains characteristic C–O (primary alcohol), Ar–O, aromatic overtones, aromatic C–H, and O–H bands at 1038, 1224, 1750–1909, 3059 and 3370 cm^{-1}, respectively (Fig. 1). The ^{1}H NMR spectrum recorded in $CDCl_3$ evidenced resonance signals of protons of relative intensities corresponding to the number and type of protons (Fig. 2).

The synthesis of naphthoxazine macromonomer of PCL (PCL-N-a) depicted in Scheme 3, involved the reaction of N-a-OH with ε-caprolactone (ε-CL) in the presence of stannous octoate catalyst.

The results of the polymerization are given in Table 1. In our experiments, the amount of $Sn(Oct)_2$ catalyst was deliberately kept low so as to prevent side-reactions such as intra- and inter-molecular transesterification [25].

As can be seen from Table 1, there is some discrepancy between the measured and ^{1}H NMR calculated M_n values. It is known that the true M_n determined for PCL is lower that that calculated from the polystyrene standards [26]. Similar observation was made by Su et al. for the benzoxazine functional PCL [27]. In Fig. 3(a) the ^{1}H NMR spectra of the polymer can be found not only the specific signals of PCL but also absorptions relating to the naphthoxazine. For instance, the characteristic peaks of an oxazine ring can clearly be seen at 4.93 ppm (N–CH_2–O) and 4.35 ppm (Ar–CH_2–N), in addition to the aromatic protons of naphthyl group appearing at between 6.98 and 7.77 ppm.

Incorporation of naphthoxazine groups was further evidenced by FT-IR spectral measurements. Fig. 4 shows

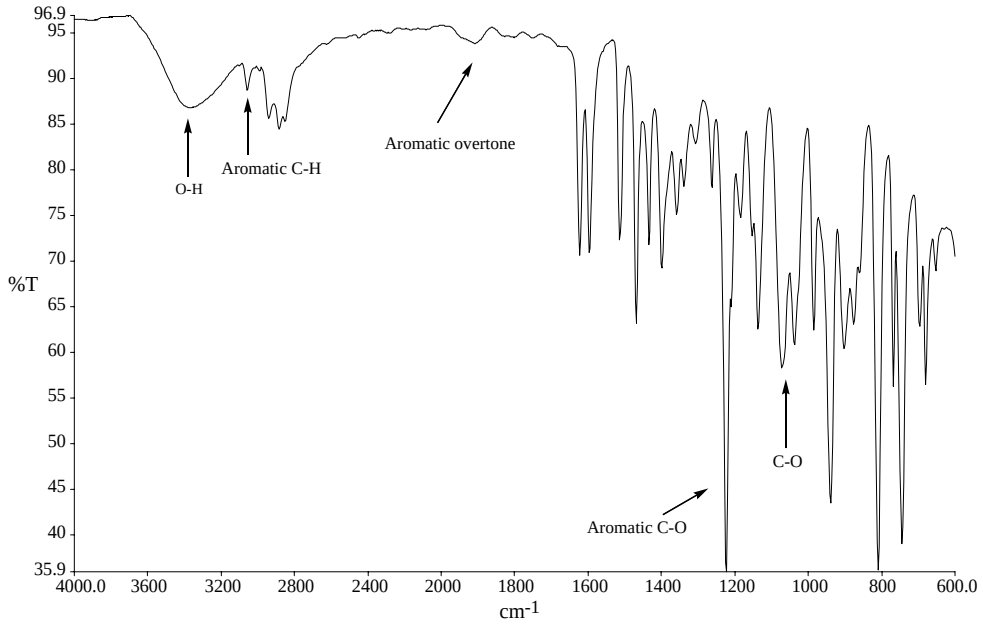


Fig. 1. FT-IR spectrum of 2-(1H-naphtho[1,2-e][1,3]oxazin-2-yl)-ethanol.

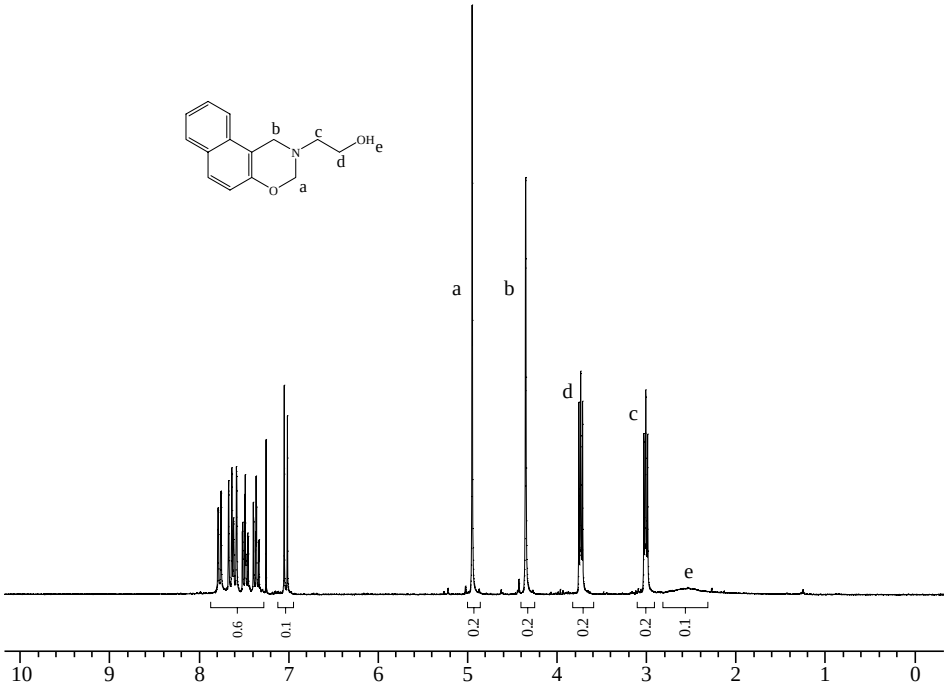
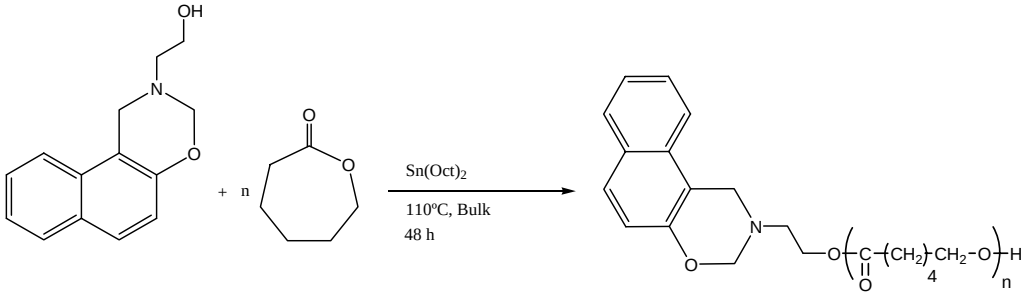


Fig. 2. ^{1}H NMR spectrum of 2-(1H-naphtho[1,2-e][1,3]oxazin-2-yl)-ethanol.



Scheme 3.

Table 1
Conditions and results of ROP of ε-caprolacton

PCL	[N-a-OH]/[CL]	$M_{nH\ NMR}$	M_{nGPC}[a]	PDI
P1	1/20	5790	7020	1.45
P2	1/30	7830	9890	1.30

$T = 110$ °C; bulk, 48 h; $Sn(Oct)_2 = 2.5 \times 10^{-6}$ mol.
[a] Determined by GPC against PS standards.

the FTIR spectra of PCL without (neat) (a) and with (b) naphthoxazine end group. It can be seen that spectrum (b) contains absorption bands at 1625 and 1594 cm^{-1} (C=C aromatic vibrations) and 806 cm^{-1} (aromatic C–H out of plane deformation bands) characteristic of naphthoxazine groups which were not present in the spectrum (a).

GPC traces recorded with the macromonomer by using RI and UV detectors are shown in Fig. 5. The dual detection provided a clear evidence for incorporation of the naphthoxazine group into polymer chain since PCL is transparent at the

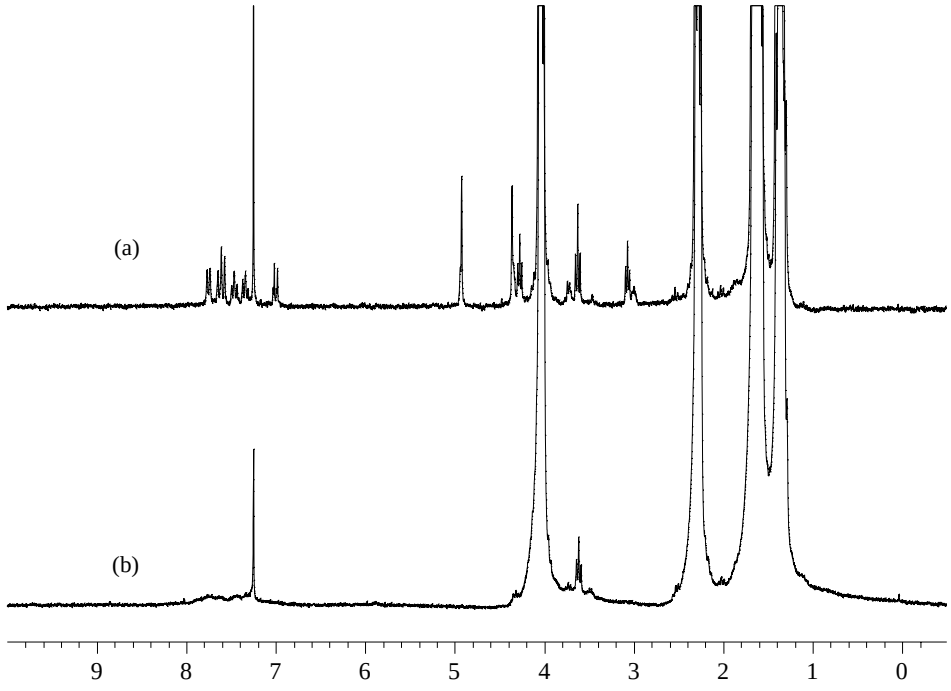


Fig. 3. ^1H NMR spectra of naphthoxazine-functional poly(ε-caprolacton) before (a) and after 1 h at 200 °C (b).

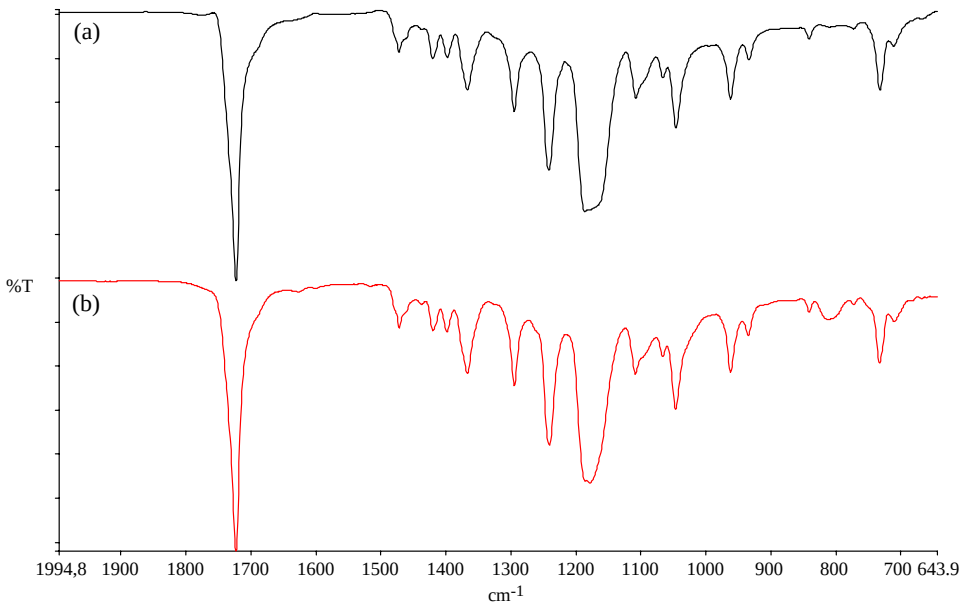


Fig. 4. FT-IR spectra of poly(ε-caprolacton) (a) and naphthoxazine-functional poly(ε-caprolacton) (PCL N-a) (b).

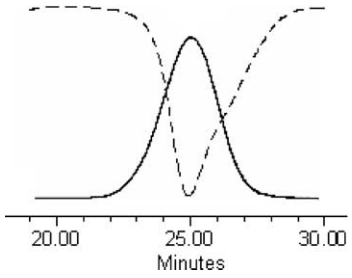


Fig. 5. GPC trace of naphthoxazine-functional poly(ε-caprolacton) (PCL N-a) (P1) by using RI (—) and UV (- - -) detectors.

wavelength (335 nm) of the UV detector. Fig. 6 shows the fluorescence excitation and emission spectra of the naphthoxazine macromonomer in chloroform at room temperature. Because of the fact that only one naphthoxazine groups is present at the polymer chain end, rather weak signals were observed. However, both spectra show the vibration structures of the naphthalene chromophore indicating that naphthoxazine groups were conserved under the polymerization conditions.

As stated previously naphthoxazine groups are expected to undergo ring opening polymerization on heating in a similar manner to benzoxazine monomers. Because of the polymeric nature, the ring opening process could not be monitored

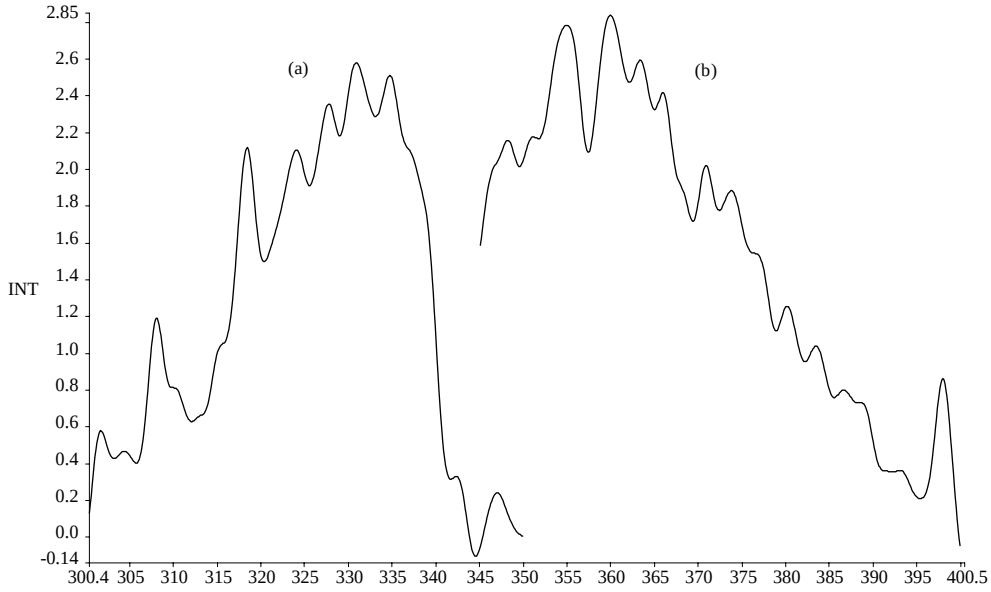


Fig. 6. Fluorescence excitation and emission spectra of the naphthoxazine functional poly(ε-caprolacton) (PCL N-a) (P1 in Table 1, 6.5 g/l) in $CHCl_3$. $\lambda_{exc}=335$ nm, $\lambda_{emis}=360$ nm.

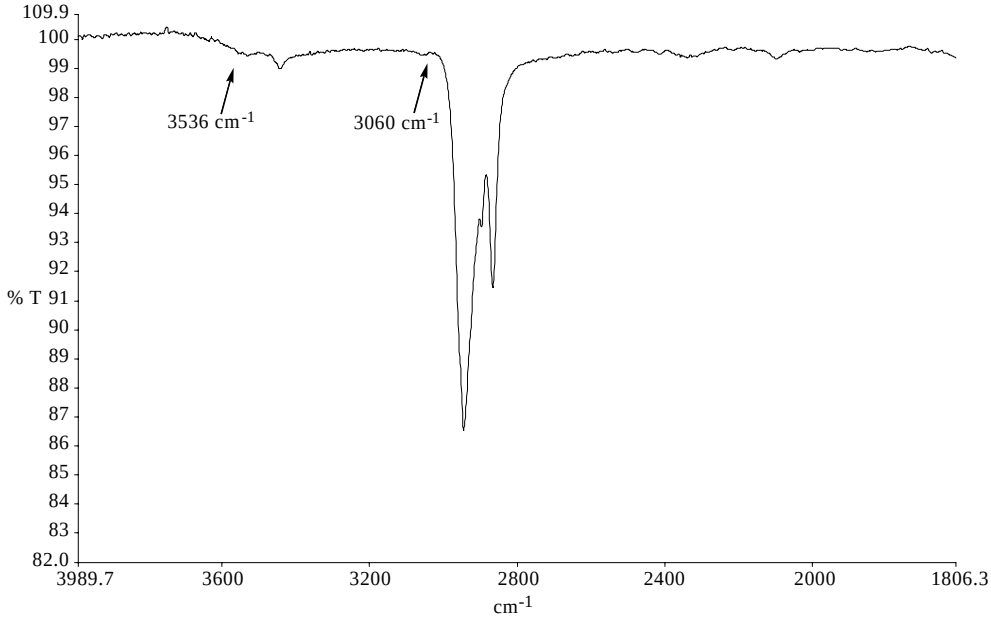


Fig. 7. FT-IR spectrum of naphthoxazine-functional poly(ε-caprolacton) (PCL N-a) after thermal treatment at 200 °C for 1 h.

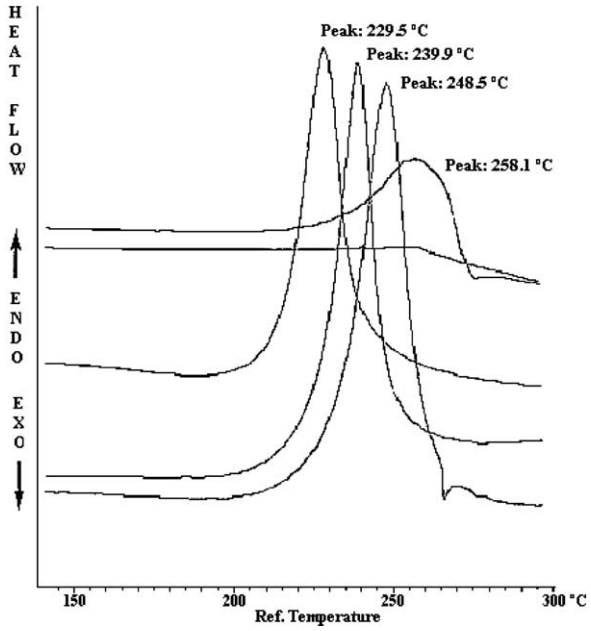


Fig. 8. DSC traces of PCL with naphthoxazine end group and benzoxazine monomer (P-a) blends; (1) 100% PCL with naphthoxazine end group (PCL N-a); (2) 75% PCL N-a, 25% P-a; (3) 50% PCL N-a, 50% P-a; (4) %25 PCL N-a, 75% P-a; (5) 100% P-a.

neither by the disappearance of the benzoxazine mode in IR spectrum nor by the exothermic peak observed in DSC thermograms. In this connection, it should be pointed out that the benzoxazine functional PCL macromonomers also do not exhibit the exotherms that observed with low molecular weight benzoxazines [27]. However, ^{1}H NMR and FT-IR investigations confirm the ring opening of the naphthoxazine groups. In the NMR spectrum of the PCL-N-a after 1 h at 200 °C, the disappearance of the benzoxazine ring and broadening of aromatic peaks belonging to naphtyl group are clearly observed (Fig. 3(b)). As can be seen from the FT-IR spectrum of the cured PCL-N-a, the phenolic O-H band at 3536 cm^{-1} and aromatic C–H stretching vibrations of naphthyl group at 3060 cm^{-1} are evidencing both incorporation and ring opening polymerization of naphthoxazine groups (Fig. 7).

We have also studied the curing behavior of the blends. DSC thermograms of the benzoxazine monomer (P-a)/(PCL-N-a) blends for various PCL-N-a concentrations are shown in Fig. 8. Only one exothermic peak was found for all concentrations which is similar to the benzoxazine monomer and its blend with neat PCL [9]. However, the curing exothermic peak shifts toward a higher temperature as the concentration of PCL-N-a increases. As both the onset and peak temperatures appear at higher temperatures as more PCL macromonomer is added into the benzoxazine monomer, the ring opening polymerization can be considered as delayed process.

Even though the macromonomer also contains naphthoxazine end groups, the concentration of polymerizable groups is diluted with by PCL component and it becomes more difficult to develop the network structure. Similar trend was also observed with the neat PCL blends [9]. It was shown that the cured products of such blends exhibit hydrogen bond formation between the hydroxyl groups of polybenzoxazine and the carbonyl groups of PCL. In our case, in addition to such interactions, PCL segments are chemically bound to the network since naphthoxazine groups also polymerize during the thermal process. Indeed, treatment of the cured product with THF and dichloromethane, which are known as solvents for PCL did not remove any polymer. Moreover, the IR spectra of this product exhibited characteristic carbonyl band at 1728 cm^{-1} indicating successful incorporation of PCL segments. When this spectrum is compared with that of the thermally

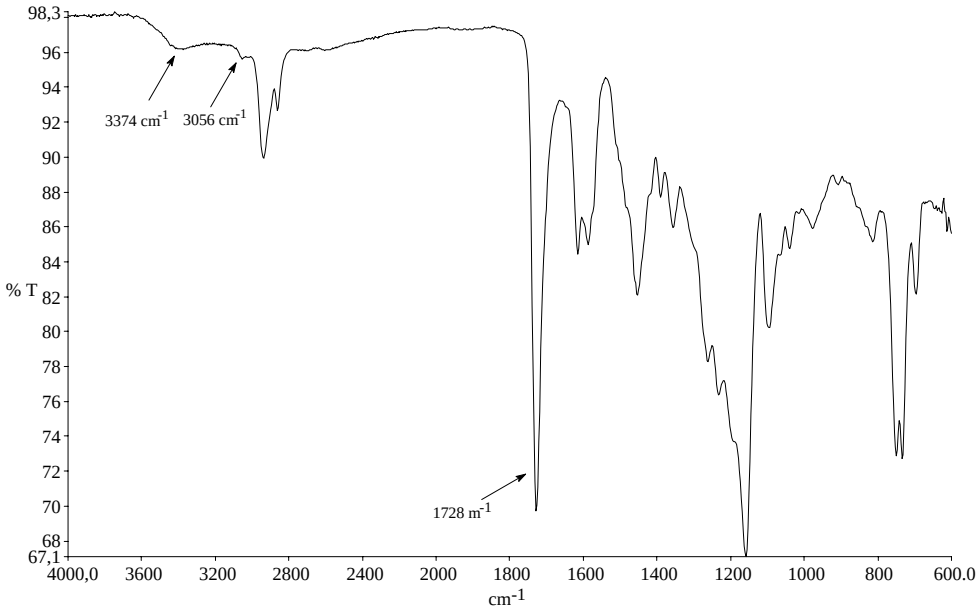


Fig. 9. FT-IR spectrum of the naphthoxazine functional poly(ε-caprolacton) PCL N-a with P-a (50/50%) after curing.

polymerized macromonomer in the absence of added benzoxazine (vide antre, Fig. 7) OH band shifts from 3536 to 3374 cm^{-1}. This shift may be due to the increased hydrogen bonding introduced by the additional benzoxazine monomer. In the spectrum aromatic C–H stretching vibration is also noted (Fig. 9).

In conclusion, naphthoxazine type PCL macromonomers were prepared by ring opening polymerization of ε-CL using $Sn(Oct)_2$ via corresponding alkyl octoate formation. Such prepared narrowly distributed macromonomers undergo thermal ring opening polymerization. When used in conjunction with conventional benzoxazine monomers, the cured products contain chemically incorporated PCL segments, which may significantly influence physical and mechanical properties. Further studies in this line are now in progress.

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