Synthesis and Thermal Characterization of Macromonomeric Azo Initiator Containing Poly(ε-caprolactone): Styrene and Methyl Methacrylate Copolymerization

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ABSTRACT: Macromonomeric azo initiator containing biodegradable poly(ε-caprolactone, (PCL) was synthesized by the condensation reaction of PCL with 4,4′-azobis(4-cyanopentanoyl chloride) and methacryloyl chloride. This macromonomeric azo initiator (MIM–PCL) was further used in the polymerization of styrene (St) or methylmethacrylate (MMA) via a radical initiated process at 60°C in bulk in order to obtain polystyrene (PS)-*b*-PCL or poly(methyl methacrylate) (PMMA)-*b*-PCL crosslinked block copolymers. Thermal decomposition kinetics of MIM–PCL and its copolymers were studied by using thermogravimetric analysis and differential scanning calorimetry (DSC). DSC traces of MIM–PCL showed two different exotherms, at 98 and 127°C. The first exotherm, observed at 98°C, was due to the polymerization of the terminal methacrylic groups; the other was due to the exothermic decomposition of azo groups of MIM–PCL. PCL-*b*-PS and PCL-*b*-PMMA crosslinked block copolymers showed single glass transition temperatures due to the compatibility of the crosslinked block segments. The polymer–solvent interaction parameter of PCL in chloroform was determined by vapor pressure osmometry to be 0.1 for the PCL–chloroform system at 30°C. The average molecular weights between junction points of crosslinked homo PCL were calculated by using the Flory–Rehner equation. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1149–1157, 1998

Key words: PCL; macroinitiator; crosslinked block copolymer; biodegradable copolymer

INTRODUCTION

Macrointermediates such as macroinitiators, macromonomers, and macrocrosslinkers have been widely used for preparing various block and graft copolymers and their networks via a radical initiated process.[1–12] Laverty and Gardlund[1] first prepared block copolymers having vinyl chloride and ethylene oxide block segments via the thermal decomposition of poly(ethylene glycol) (PEG)-based macro azo initiators (MAIs) having several azo groups in the presence of vinyl chloride monomer. Walz and colleagues[2] have reported polyazoester (PAE), synthesis from the reaction of PEG and
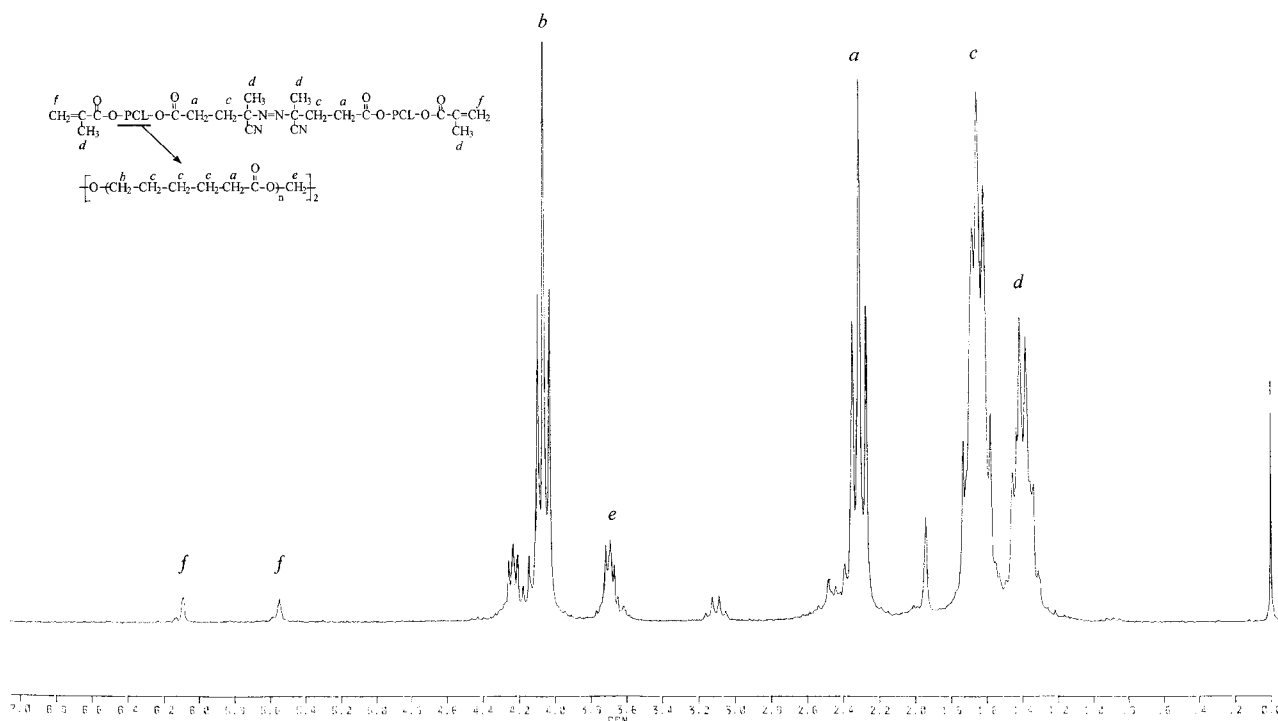
Figure 1 NMR spectrum of MIM–PCL.

azobisisobutyronitrile in the presence of dry HCl according to Pinner's synthesis.[2] Haneda and associates reported on the linear styrene (St) and methyl methacrylate (MMA) copolymers of MAIs composed of various polyesters.[8] Recently a new kind of macrointermediate, macromonomeric azo initiators (MMAIs), containing PEG units have been reported by Hazer.[5–7] These were synthesized by the capping reaction of —OH end groups of PAEs with methacryloyl chloride, isocyanatoethyl methacrylate, or 4-vinyl benzyl chloride. The homopolymerization or copolymerization of MMAI with a vinyl monomer yields a branched or crosslinked block copolymer, depending on its concentration and polymerization time.

Recently, due to increasing awareness of and sensitivity on environmental problems arising from using large quantities of engineering plastics in our daily living, intense demand for the synthesis of biodegradable polymers and their copolymers and blends has been growing.[13–17] Poly(ε-caprolactone) (PCL) has been spotlighted as a biodegradable polyester because of its morphologic and physical properties, and its miscibility with some important engineering plastics. PCL also has a relatively low cost, sufficient water and hydrolytic resistance, and selective microbial degradation.[18] Therefore much work has been de-

voted to preparing linear and well-defined linear block copolymers of PCL with St and siloxane via anionic polymerization.[13–15]

The object of this study was to synthesize a new kind of MMAI based on PCL units (MIM–PCL) and to investigate the thermal behavior of PCL-b-polystyrene (PS) or PCL-b-poly-(methyl methacrylate) (PMMA) crosslinked block copolymers obtained by vinyl copolymerization with MIM–PCL.

EXPERIMENTAL

Materials

PCL was purchased from Polyscience (USA) and used without further purification. Its molar mass and hydroxyl functionality were 1250 g/mol and 2.0, respectively. 4,4′-Azobis(4-cyanopentanoic acid) (ACPA) was purchased from Fluka AG (Switzerland) with better than 98% purity. ACPA was converted to the acid chloride derivative 4,4′-azobis(4-cyanopentanoyl chloride) (ACPC) having a melting point of 97°C according to the method of Cowie and Yazdani-Pedram.[4] Methacryloyl chloride was purchased from Fluka AG. St and MMA were purified in the conventional
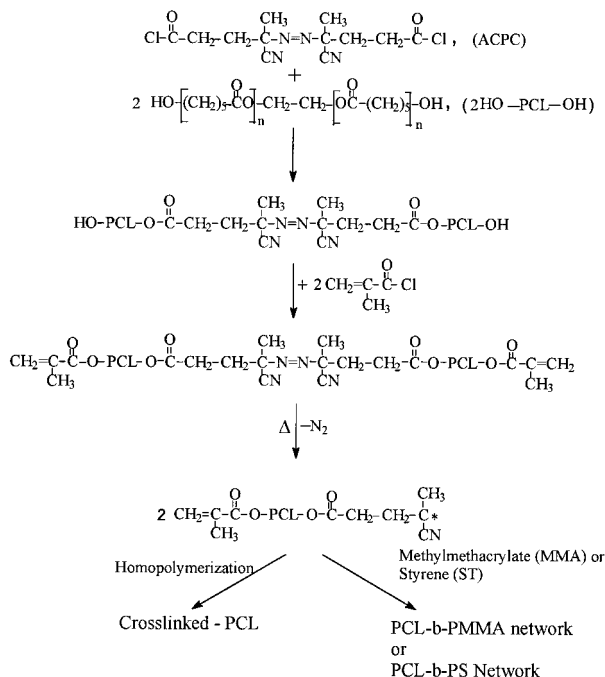
Scheme 1

manner. Ethylene glycol dimethacrylate (EGDM) was purchased from Merck (Germany) with better than 98% purity and used as received.

Instrumentation

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements were carried out by using a DuPont DSC-9100 and DuPont TGA-951, respectively, with a TA-9900 data processing system under nitrogen atmosphere. The DSC was calibrated with metallic indium (99.99% purity) and TGA calibrated with calcium oxalate. For spectroscopic measurements a Perkin–Elmer 177 infrared (IR) spectrometer and a 200 MHz Bruker-AC 200L NMR spectrometer, using $CDCl_3$ as solvent, were used. To determine the number-average molecular weight and polymer–solvent interaction parameter (χ_1) for the PCL–chloroform system, a Knauer type vapor pressure osmometer (VPO) was used. VPO measurements were carried out at 30°C in chloroform.

Synthesis of PCL Macroinitiator (MI–PCL)

MI–PCL was synthesized by using the procedure cited by Haneda and coworkers.[8] A solution of 20 mmol of PCL having terminal —OH groups and

20 mmol of triethyl amine in 75 mL of methylene chloride was prepared. A separate solution of 10 mmol of ACPC in 50 mL of methylene chloride was gradually added to this solution at 0°C in 30 min. After 3 h stirring, the solution was allowed to warm up to room temperature and was stirred overnight in the dark. After 24 h stirring, the solution was filtered and washed with 15% HCl aqueous solution to remove the triethylamine hydrochloride complex and was dried over Na_2SO_4. After filtration, solvent was partly evaporated and the MI–PCL was precipitated in petroleum ether and dried at room temperature. The spectroscopic characterization of MI–PCL is as follows. Nuclear magnetic resonance (NMR): δ (ppm) = 1.7 and 2.3–2.7 (d, CH_3— and m, CH_2— groups of azobis cyanopentanoyl, respectively), 3.6–3.8 (m, O—CH_2 groups of PCL); IR (cm^{-1}) = 3500 and 1730 (HO— and C=O groups of MI–PCL, respectively).

Synthesis of PCL Macromonomeric Initiator (MIM–PCL)

A mixture of 40 mmol methacryloyl chloride and 75 mL of methylene chloride was gradually added into the mixture of 20 mmol MI–PCL, 20 mmol triethyl amine, and 75 mL methylene chloride, in 30 min at 0°C. After 3 h stirring, the solution was allowed to warm up to room temperature and stirring was carried out at room temperature

(A)
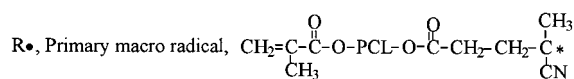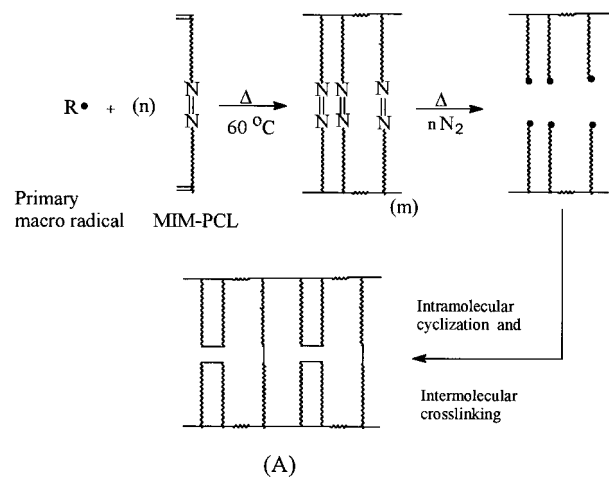
Scheme 2

Table I   Copolymerization and Swelling Experiments: Data on Styrene and Methyl Methacrylate with MIM–PCL

Run No.	MMAI		Vinyl Monomer		Yield of Crosslinked Copolymer		Equilibrium Swelling Ratio (q_v)
	Type	Amount (g)	Amount (g)	Type	(g)	(wt %)	
1	MIM–PCL	1.0026	—	—	0.7759[a]	77.39	9.9
2	MIM–PCL	1.0004	8.0003	MMA	9.0000	100.00	7.0
3	MIM–PCL	1.0521	5.0022	MMA	5.9125	97.65	7.2
4	MIM–PCL	1.0000	1.0033	MMA	1.5670	78.22	8.1
5	MIM–PCL	1.0082	0.3066	MMA	0.8314	63.23	8.5
6	MIM–PCL	1.0031	5.0000	St	2.3894	39.80	21.8
7	MIM–PCL	1.0006	2.0012	St	1.5305	51.00	19.1
8	MIM–PCL	1.0058	1.0166	St	1.6520	81.69	13.7
9	MIM–PCL	1.0065	0.3005	St	1.0487	80.24	12.9

Copolymerization was carried out in bulk at 60°C for 3 h, and the swelling experiments were carried out in chloroform at 30°C.
[a] Only homopolymer network (A) shown in Scheme 2.

overnight in the dark. MIM–PCL was isolated by the same procedure described above for MI–PCL and the yield was 93%. IR (cm^{-1}) = 1730 and 1630 (C=O and terminal —CH$_2$=CH$_2$ groups, respectively. The NMR spectrum of MIM–PCL is shown in Figure 1. The common characteristic peaks of both MI–PCL and MIM–PCL are seen in this figure. The methacrylic groups content of MIM–PCL was determined as 1.80 equivalent/ mol using a bromometric method.[19] This method is based on the bromination of double bonds of methacrylic groups with pyridinium sulphate dibromide and back-titration of excess bromine. The bromination method is reported to be capable of strikingly accurate results.[19] Scheme 1 indicates the whole reaction, including the synthesis of MIM–PCL.

Homopolymerization of MIM–PCL

Homopolymerization of MIM–PCL was carried out at 60°C for 3 h in an argon atmosphere (Scheme 1) and the yield was calculated gravimetrically. The production of primary macroradicals, the polymerization of methacrylic groups, cyclization, and crosslinking reaction are shown in Scheme 2.

Copolymerization of Vinyl Monomers with MIM–PCL

MIM–PCL contains two terminal methacrylic groups, located at each end of the chain, and one azo group in the middle of the molecule. MIM–

PCL initiates a block copolymerization in the presence of another vinyl monomer, which yields the crosslinked copolymer. The copolymerization step is also included in Scheme 1. For the bulk polymerization of St and MMA, MIM–PCL was dissolved in one of these monomers in a Pyrex tube in different compositions. The contents of the reaction tubes were flushed with argon, capped with rubber septums, and immersed in an oil bath at 60°C for 3 h.

Swelling of the Networks

To calculate the average molecular weight between junction points ($\overline{M}_c$) of crosslinked homopolymer [network (A) in Scheme 2] and characterize the copolymeric networks, their swelling test was carried out in chloroform at 30°C. Swelling results are gathered in Table I. The swelling ratio of the MIM–PCL network and its copolymers at equilibrium was calculated gravimetrically according to the following equation[20]:

$$q_v = 1 + (w_2/w_1 - 1)\rho_2/\rho_1$$

where, q_v is the equilibrium swelling ratio by volume, w_2 is the weight of the swollen sample at equilibrium, w_1 is the weight of the sample in dry state, and ρ_1 and ρ_2 are the densities of polymer and solvent, respectively. Depending upon the proportions of MIM–PCL and monomer in the network structure (see Table I), the densities of dry copolymer networks were calculated from the
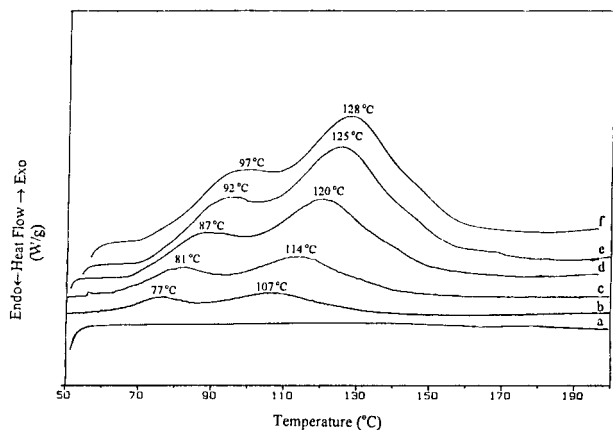
Figure 2 DSC curves of PCL (a) and MIM–PCL taken under various heating rates: (b) 2°C/min; (c) 4°C/min; (d) 8°C/min; (e) 12°C/min; (f) 15°C/min.

densities of monomers and PCL using the following equation:

$$\rho_2 = X\rho_{\mathrm{MIM-PCL}} + (1 - X)\rho_M$$

where X is the weight fraction of MIM–PCL, and $\rho_{\mathrm{MIM-PCL}}$ and ρ_M are the densities of MIM–PCL and monomer, respectively.

Thermal Studies

Thermal stability of homopolymeric network (A), crosslinked PCL-*b*-PMMA, and PCL-*b*-PS block copolymers were determined by using TGA techniques under nitrogen atmosphere at heating rate of 10°C/min according to the Freeman and Carrol method.[21] Activation energies of the methacrylic polymerization and decomposition of the azo group in MIM–PCL were determined by using the DSC technique according to the Ozawa method[22] at a heating rate of 2, 4, 8, 12, and 15°C/min. The glass transition temperature (T_g) values of block copolymers were determined at 10°C/min by DSC.

RESULTS AND DISCUSSION

The experimental results on homopolymerization of MIM–PCL and copolymerization of St or MMA with MIM–PCL appear in Table I. In this table the yields of homopolymeric and copolymeric networks are collected.

$\bar{M}_c$ value and the degree of crosslinking are the main characteristic parameters for any network.

Therefore the $\bar{M}_c$ value of the PCL network [(A) in Scheme 2] obtained by the homopolymerization of MIM–PCL was determined by using the Flory–Rehner equation from the equilibrium swelling data in chloroform. Before attempting to use this equation, the Flory–Huggins interaction parameter of polymer–solvent system χ_1 was first determined as 0.1 for the PCL–chloroform system using VPO according to the methods cited.[23–25] Using the equilibrium swelling value of the PCL network and the χ_1 parameter of the PCL–chloroform system (see Table I), the $\bar{M}_c$ value of the PCL network was calculated by using the following Flory–Rehner equation:

$$\bar{M}_c = -v_1\rho(v_{2m}^{1/3} - v_{2m}/2)/[\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2]$$

where $\bar{M}_c$ is the average molecular weight between junction points, v_1 is the molar volume of solvent, ρ is the density of the PCL network, and v_{2m} is the volume fraction of polymer in the gel at equilibrium ($v_{2m} = 1/q_v$). By using the polymer–solvent interaction parameter (χ_1) for the PCL–chloroform system obtained from VPO, and the swelling result of crosslinked homopolymer (A)
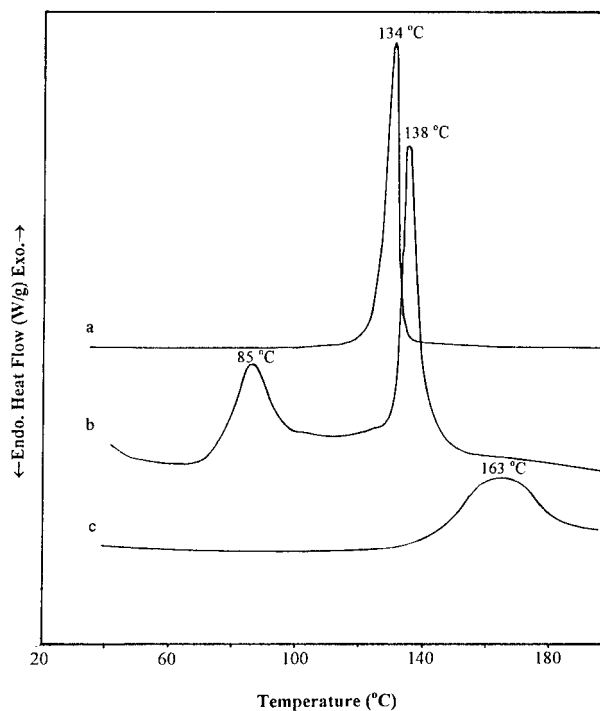

Figure 3 DSC curves of ACPA, EGDM, and the model mixtures of ACPA and EGDM. (a) ACPA; (b) ACPA + EGDM; (c) EGDM.
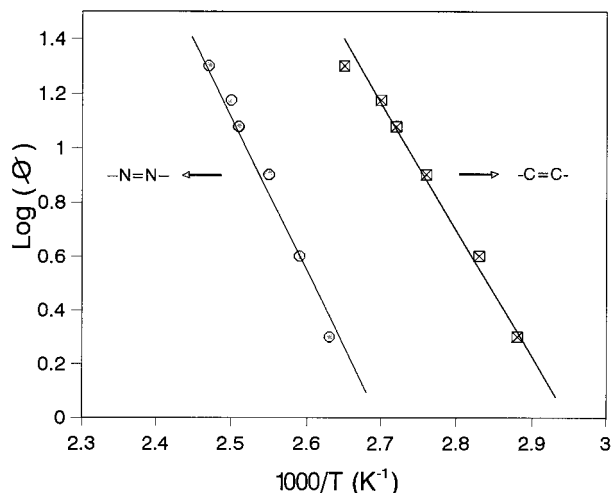
Figure 4 Plot of the heating rate versus reciprocal peak temperatures of the exotherms shown in Figure 2. (⊠) First exotherm; (●) second exotherm.

in chloroform, the $\bar{M}_c$ of the PCL network was calculated as 8000 g/mol through the Flory–Rehner equation.[26-28] If we take into account the contribution of the ACPA, methacryloyl chloride, and the number average molecular weight of PCL prepolymer, the calculated $\bar{M}_c$ value of this chain would be nearly 3000 g/mol (see Scheme 1). The $\bar{M}_c$ value of the final network, determined from swelling experiments using the Flory–Rehner equation, is significantly different from calculated $\bar{M}_c$ value. This difference may be due to the probable chain extension taking place during the polymerization of methacrylic groups within MIM–PCL chains and also to formation of cyclization in the course of thermal decomposition of the azo

groups of ACPA (see Scheme 2). The cyclic structure does not contribute to the elastic activity of the network. Therefore the $\bar{M}_c$ value obtained from swelling data seems to be higher than expected. This observed difference cannot be attributed only to the above side reaction, since VPO is not an absolute method of determining χ_1 parameter unequivocally for this system; and also because $\bar{M}_c$ found using the Flory–Rehner equation is an approximate quantity.

For the copolymerization of MIM–PCL with St or MMA, four different compositions of vinyl monomer to macroinitiator (MIM–PCL) were chosen. Table I clearly shows that, as the MMAI content of the copolymerization mixture is increased, the polymerization yield increased and the degree of equilibrium swelling for copolymer networks decreased. It can be seen from the swelling data that the swelling of the networks is effected by the type of block segment (MMA or St) and its ratio to the MIM–PCL. For the same monomer/MIM–PCL ratios of the St and MMA (Table I, runs 3 and 6), the PMMA-containing networks have the smaller swelling values but higher conversions. These results are due to the differences in the solubility in chloroform and the reactivity of both monomers. It is very interesting to see that, as the PMMA content of any copolymeric network decreases, swelling of the network increases, whereas the opposite of this is observed for the PCL–PS networks. This may be explained by the solubility differences; there may also be an effect from termination reactionsof radical polymerization of MMA and St. Since both monomers could be terminated by

Table II Kinetic Parameters of the Thermal Decomposition of MIM–PCL and Its Copolymers

Run No. (from Table I)	Structure Type	Activation Energy (kJ/mol)	Preexponential Factor (min^{-1})	Maximum Weight-Loss Rate Temperature[a] (°C)	Rate Constant[b] k (min^{-1})
1	MIM–PCL—N=N—	113.8	8.69×10^{14}	122	1.33×10^{-3}
	—C=C—	79.9	1.48×10^{11}	89	4.59×10^{-2}
3	PCL-*b*-PMMA	133.4	1.71×10^{10}	406	0.93
4	PCL-*b*-PMMA	139.8	1.55×10^{10}	409	0.21
5	PCL-*b*-PMMA	142.1	1.03×10^{10}	413	0.24
6	PCL-*b*-PS	225.9	1.97×10^{16}	424	0.23
8	PCL-*b*-PS	217.5	2.99×10^{15}	425	0.16
9	PCL-*b*-PS	193.1	1.14×10^{14}	426	0.42
10	Homo-PCL	190.0	5.37×10^{14}	421	2.68

[a] Maximum decomposition rate temperatures were determined by using TGA for runs 3–10, DSC for run 1.
[b] Rate constants were determined at 60°C for run 1, and at maximum decomposition temperature for runs 3–10.

Table III T_g **Values of Crosslinked Block Copolymers and Their Calculated Compositions**

Run No. (from Table I)	Copolymer Type	T_g (°C)	PS or PMMA Content in Network[a] (wt %)
3	PCL-*b*-PMMA	63	83 PMMA
4	PCL-*b*-PMMA	5	51 PMMA
5	PCL-*b*-PMMA	−46	10 PMMA
6	PCL-*b*-PS	55	81 PS
8	PCL-*b*-PS	10	56 PS
9	PCL-*b*-PS	−45	11 PS

[a] Calculated from the Fox equation $1/T_g = w_1/T_{g1} + w_2/T_{g2}$, $T_{g1} = -55°C$ for PCL, $T_{g2} = 105°C$ for PMMA and 100°C for PS.

either disproportionation or combination, this would introduce structural irregularities into both copolymeric networks.

Thermal Characterization

MAIs are well known as initiators in the radical-initiated copolymerization of vinyl monomers. In the course of polymerization they produce macroradicals accompanying N_2 elimination. The thermal stability of the MIM–PCL greatly affects the polymerization yield and therefore, in order to determine the kinetic parameters of MIM–PCL, its DSC thermograms obtained at different heating rates were recorded [Fig. 2(b–f)]. In Figure 2, the DSC thermograms of MIM–PCL show two characteristic exothermic peaks, whereas the DSC thermogram of homo-PCL does not have an exotherm [Fig. 2(a)]. As expected, peak temperatures shifted to higher values as the heating rate was increased.

In order to elucidate the exothermic two-stage thermal behavior of MIM–PCL, first, the DSC and TGA traces of ACPA were recorded at 10°C/min heating rate. In the DSC thermogram of ACPA [Fig. 3(a)], a sharp and narrow exothermic peak, which is due to exothermic decomposition of azo groups of ACPA, was observed at 134°C. This exothermic peak coincides with the first-stage weight-loss step of ACPA obtained from its TGA thermogram, which was observed at around 134°C. These results are proof of the decomposition of azo groups of ACPA that is observed at around 134°C. It is evident from the thermograms of ACPA that the upper exothermic peak shown in Figure 2 is due to the exothermic decomposition of azo groups of MIM–PCL, which is in the middle of the chain. The lower exothermic peak shown in Figure 2 is due to the polymerization of the termi-

nal methacrylic groups initiated by the primary radicals forming in the early stage of the decomposition of azo groups, being in the middle of the MIM–PCL chains. With an aim of better understanding the two-stage decomposition process of MIM–PCL, a stoichiometric mixture of EGDM and ACPA was prepared (1 : 1 by mol ratio of EGDM and ACPA). The DSC curves of the stoichiometric mixture and pure EGDM were recorded separately [Fig. 3(b, c)]. The DSC thermogram of the stoichiometric mixture has two exotherms, at 85 and 138°C [Fig. 3(b)]; this is similar to the DSC thermograms of MIM–PCL shown in Figure 2. The DSC thermograms of pure EGDM [Fig. 3(c)] showed only one broad exothermic peak at around 163°C, extending over the range of 135–180°C, which is due to the thermally initiated polymerization of terminal methacrylic groups of EGDM. These DSC thermograms provide further proof that the first exotherm is due to the polymerization of the terminal methacrylic group initiated by macroradicals produced from decomposition of the azo groups.

The kinetic activation energy, due to the decomposition of both azo groups and consecutive polymerization of the terminal double bonds of MIM–PCL, was obtained using DSC. This was determined from the plot of the logarithm of the heating rate versus reciprocal maximum peak temperatures (Fig. 4). According to the Ozawa method, the relationship between heating rate and temperature is as follows[22]:

$$\log \beta = \alpha(1/T) + \beta$$

$$\alpha = -0.457\Delta E/R$$

where β is the heating rate, T is peak temperature (K), ΔE is kinetic activation energy, and R is the

gas constant. The slope of the lines in Figure 4 gives us the value of α. The activation energy values were calculated as 113.8 kJ/mol for decomposition of azo groups. This result is consistent with the earlier findings of Haneda and colleagues[8] (for PCL-based macroinitiator, MI–PCL, it is 110.1 kJ/mol), where it was reported that the activation energy values of the azo group in the different macroazoinitiators are almost the same. The thermal decomposition kinetics of azo initiators have been studied by various authors.[29] Using the same procedure, the opening activation energy of the terminal double bonds was determined as 79.9 kJ/mol. It is interesting to note that the polymerization of the methacrylic group has a lower activation energy than that of azo group decomposition. The calculated rate values are also included in Table II. These results imply that the methacrylic group polymerization, corresponding to the first exotherm shown in Figure 2, is completed before azo group decomposition. Taking these kinetic activation energy results and the calculated $\bar{M}_c$ value of the PCL network into consideration, we propose the reactions shown in Scheme 2 as a possible route to the homopolymerization of MIM–PCL.

In the TGA thermogram of the PCL network, the temperature of the maximum weight-loss rate was observed at 421°C. Some characteristic parameters, obtained from TGA measurements, are collected in Table II. As shown in Table II, increasing the PCL content of the crosslinked block copolymers (runs 3–5 in Table II) caused a considerable increase in the maximum weight-loss rate temperature of PCL–b–PMMA copolymers. This tendency has not been observed for the PCL-b-PS-type copolymers because homo-PCL and PS have nearly the same maximum weight-loss rate temperatures. The decomposition activation energies of crosslinked block copolymers were also calculated by TGA using the Freeman and Carroll method.[21] These results are gathered in Table II. It was observed that for PCL-b-PMMA-type copolymers, the decomposition activation energy increases with PCL content. However, for PCL-b-PS-type copolymers, a decrease in the activation energy was seen on increasing the PCL content. These findings seem to be quite reasonable, since the decomposition activation energy of homo-PCL (190 kJ/mol) is higher than pure PMMA and lower than pure PS.

For a typical block copolymer one can expect different T_gs corresponding to those of its block segments. Interestingly, in this work we observed that each type of copolymer having various compositions showed a single T_g which was between the T_g values of the corresponding homopolymers of block segments. DSC thermograms of the copolymers containing approximately 1 : 1 by weight block segments (runs 4 and 8 in Table III) displayed very broad T_g curves centered around the T_g values of corresponding homopolymers. This resulted from the overlap of the pure PCL ($T_g = -55°C$) and a PS ($T_g = 100°C$) or PMMA ($T_g = 105°C$) mixed phase near 10°C.[30] These results clearly indicate the compatibility of PCL with PS or PMMA in the crosslinked block copolymer form.

As shown in Table III, the calculated amount of the PMMA and PS in the copolymers, using the Fox equation,[31] are in good accord with the initial compositions of the copolymerization mixture shown in Table I.

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