

Macro-Azo-Initiators Having Poly(ethylene glycol) Units: Synthesis, Characterization, and Application to AB Block Copolymerization

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ABSTRACT: Macro-azo-initiators (MAIs) having poly(ethylene glycol) (PEG) units were obtained by various multistep synthetic approaches. In the first stage, macro-azo-initiators of PEG type with azo groups inserted in the main chain were prepared. MAIs were then characterized by chemical analyses, spectral methods, ¹H-NMR, GPC, and DSC techniques. They were used in the free-radical bulk polymerization of dicyclohexylitaconate to synthesize AB block copolymers of poly(ethylene glycol-*b*-dicyclohexylitaconate) (PEG-*b*-PDCHI). © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2173–2181, 1997

INTRODUCTION

Macro-azo-initiators (MAIs) provide a useful means of preparing block copolymers via free-radical polymerization.^{1–6} A variety of macro-azo-initiators and macromonomeric initiators (macroinimers) containing poly(ethylene glycol) (PEG) units were reported recently.³ Since PEG has a high hydrophilicity, flexibility, and ion absorbability, incorporation of PEG into vinyl macromolecular compounds seems to be important.^{1,3,4,6,7}

The present article deals with the synthesis of macro-azo-initiator having PEG units by using different synthetic routes. The first approach is a three-step procedure. In the first step, 4,4'-

azobis(4-cyanopentanoic acid) (ACPA) was reacted with 2,3-epoxypropyl neodecanoate (CE-10). In the second step, an aliphatic diisocyanate (isophorone diisocyanate) (IPDI) was reacted with poly(ethylene glycol) monomethyl ether (PEGMME).

The resulting products of the first and second steps were reacted in the third step. In the second approach, isocyanate-capped PEGMME was reacted with ACPA to synthesize MAI 2. The third synthetic route to apply was the reaction 4,4'-azobis(4-cyanopentanoyl chloride) (ACPC) with PEGMME to prepare MAI 3. After characterization of the MAIs, block copolymerization with dicyclohexylitaconate was carried out. AB-type block copolymers of poly(dicyclohexylitaconate-*b*-ethylene glycol) (PDCHI-*b*-PEG) were synthesized.

The properties of PEG/PDCHI blends were examined recently.^{8,9} We presumed that the study of AB-type block copolymers of PDCHI-*b*-PEG would be interesting in order to see the effect of the presence of PDCHI blocks on the morphology and crystallization properties of PEG in PEG/PDCHI blends.

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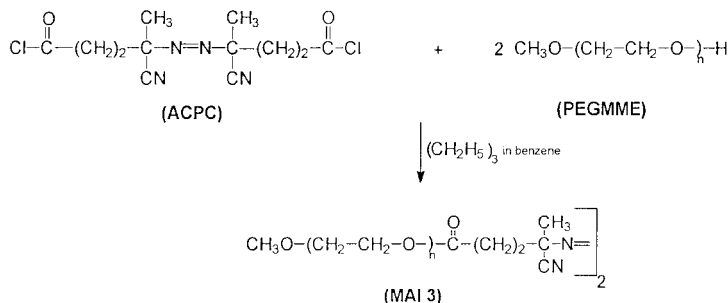
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Scheme 3 Synthesis of MIM 3.

of the end-capped products was determined by end-group titration of isocyanate.¹² Gel permeation chromatographs (GPC) were obtained on a

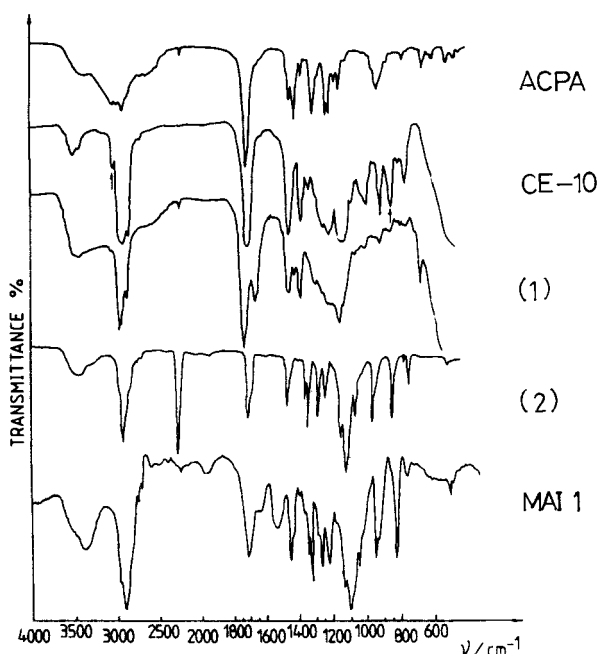


Figure 1 IR spectrum of the intermediate and resulting products in the synthesis of macro-azo-initiator MAI 1. Characteristic peaks for ACPA: OH stretching at 3500–3300 cm^{-1} , C=O st. at 1700 cm^{-1} , CH st. at 3000–2900 cm^{-1} , CN st. 2220 cm^{-1} . For CE-10: CH st. at 2960–2840 cm^{-1} , C=O st. at 1710 cm^{-1} , C—O—C st. at 1240–1200 cm^{-1} , 1300–1240 cm^{-1} , 840 cm^{-1} . CH st. at 3020 cm^{-1} . For (1), the product of step 1: OH st. at 3650–3400 cm^{-1} , CH st. at 2960–2860 cm^{-1} , C=O st. at 1660 and 1725 cm^{-1} , CN at 2220 cm^{-1} , C—O at 1150 cm^{-1} . For (2), NCO-capped PEGMME: CH st. at 2920–2840 cm^{-1} , N=C=O st. at 2300 and 1390 cm^{-1} , C=O st. 1700 cm^{-1} , NH st. 3450 cm^{-1} . For MAI 1: NH st. 3350 cm^{-1} , CH st. 2960–2820 cm^{-1} , C=O st. at 1725 cm^{-1} and C=O (amide) 1660 cm^{-1} , C—O—C st. at 970 cm^{-1} , CN at 2220 cm^{-1} .

Waters instrument. Tetrahydrofuran served as an eluent at 40°C. The flow rate was 1 mL/min. IR spectra of samples were produced using a Perkin-Elmer 983 spectrometer.

¹H-NMR spectra were recorded by using a Bruker-AC 200L, 200 MHz NMR spectrometer. DSC thermal curves were produced by in a Shimadzu DSC-41 apparatus under different heating rates.

Procedure

Synthesis of Macro-azo-initiator 1 (MAI 1)

MAI 1 was prepared by the following three-step procedure: In the first step, 4,4'-azobis(4-cyanopentanoic acid) (ACPA) was reacted with 2,3-epoxy-propyl neodecanate (CE-10) in dry dimethylformamide (DMF), in the presence of 1% TEA, at room temperature under a blanket of dry nitrogen. The reaction mixture was stirred for 48 h. The molar ratio of ACPA to CE-10 was 1 : 2.5 mol. The DMF was separated by vacuum distillation and the resulting product was poured into water and subsequently extracted with ether. The extract was dried with Na_2SO_4 , and ether was evaporated. The product was washed with petroleum ether, which is a good solvent for epoxide. The final product was a very viscous liquid. The yield was about 100%. The carboxylic group content was determined by a microtitration method.¹¹

The second step was a capping reaction of PEGMME with IPDI in benzene, under dry nitrogen on a magnetic stirrer at about 80°C for 40 h. The molar ratio of PEGMME to IPDI was 1 : 6 in order to ensure obtaining an isocyanate-capped product. The resulting product, after evaporation of benzene, was precipitated with petroleum ether and dried in a vacuum oven. The isocyanate content of the end-capped product was determined by end-group titration of isocyanates.¹²

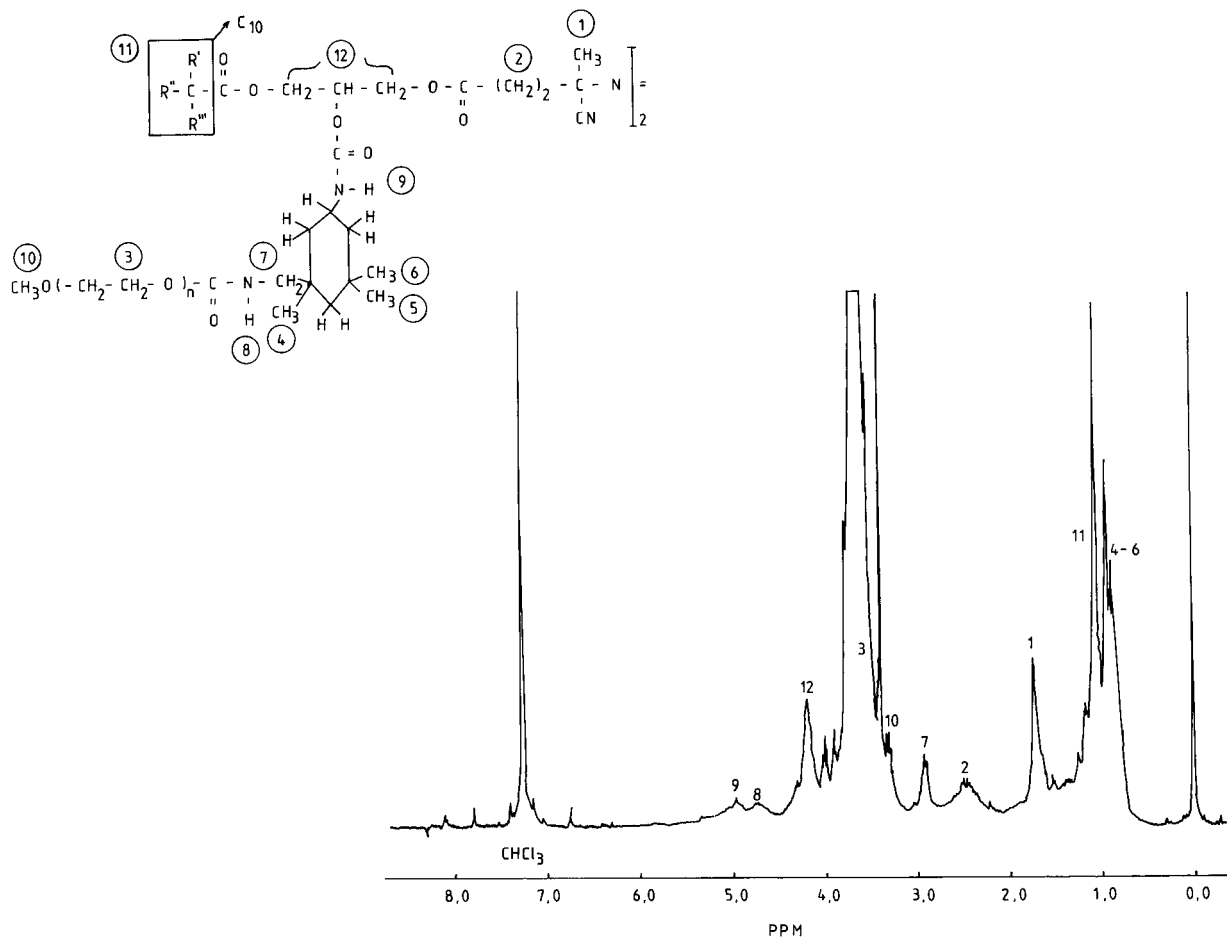


Figure 2 $^1\text{H-NMR}$ spectrum of macro-azo-initiator, MAI 1.

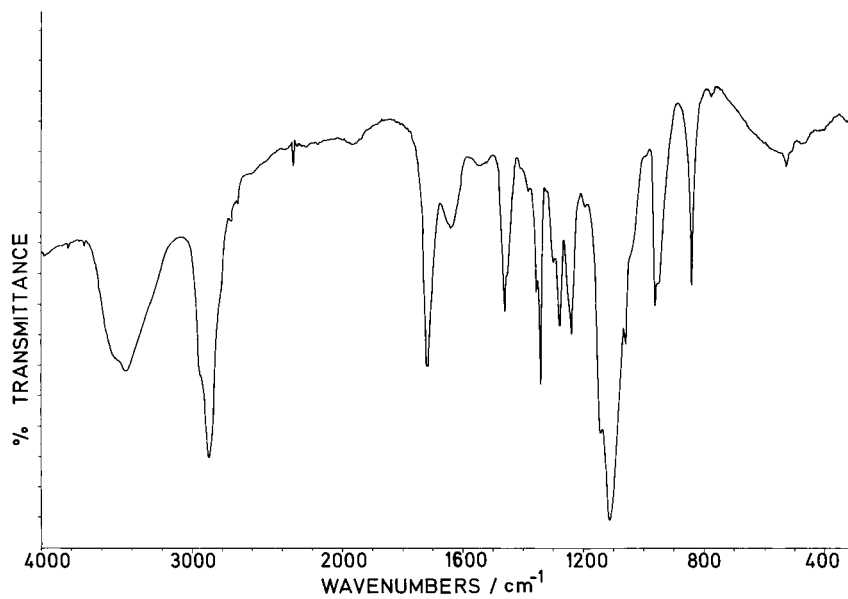


Figure 3 IR spectrum of macro-azo-initiator, MAI 2.

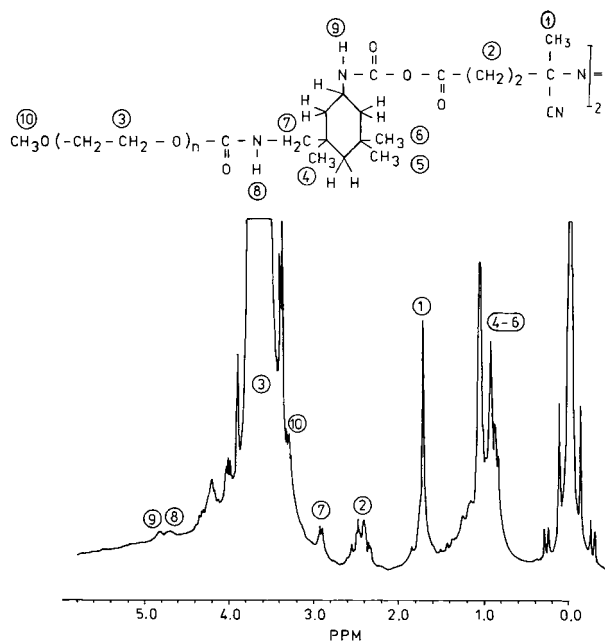


Figure 4 $^1\text{H-NMR}$ spectrum of macro-azo-initiator, MAI 2.

The third step was a coupling reaction between the products (1) and (2) of steps 1 and 2 described above. The reaction was carried out in dioxane, in the presence of several drops of the T-12 catalyst at room temperature, under dry nitrogen and for 160 h. The molar ratio of product (1) to product (2) was 1 : 2 mol. The

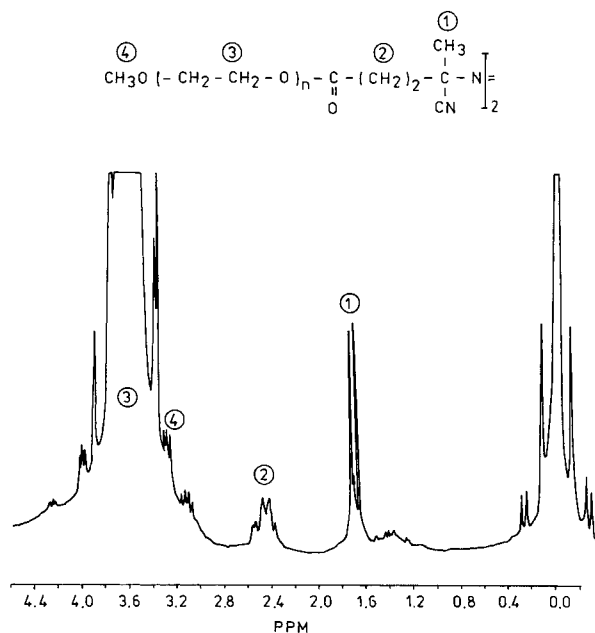


Figure 6 $^1\text{H-NMR}$ spectrum of macro-azo-initiator, MAI 3.

resulting product of the third step was precipitated from petroleum ether and washed several times with diethyl ether. The product (MAI 1) was dried in a vacuum. The disappearance of the NCO peak was observed by IR spectroscopy. The reaction steps for MAI 1 are shown in Scheme 1.

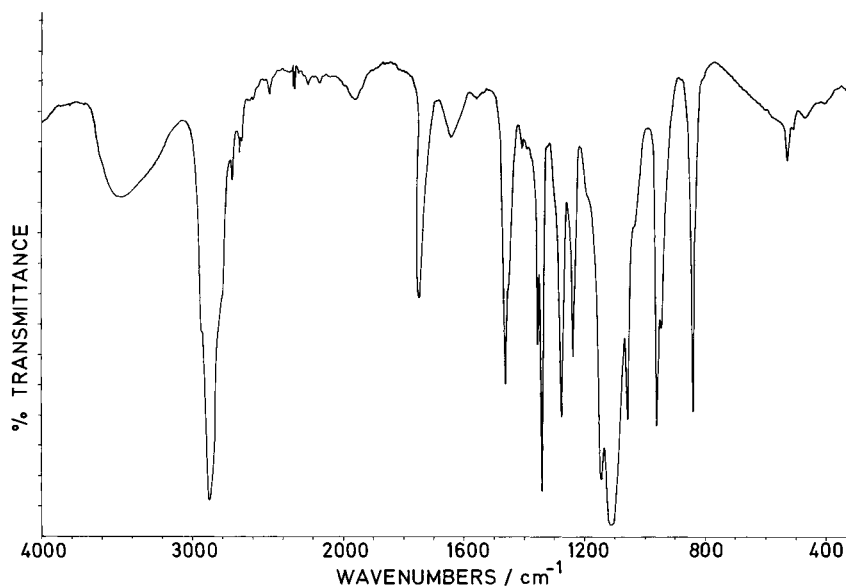


Figure 5 IR spectrum of macro-azo-initiator, MAI 3.

Table I GPC Results and Calculated Molecular Weights of MAIs

Macro-azo-initiator	M_n (g/mol)	M_w (g/mol)	M_w/M_n	M_n^{ca}
MAI 1	6010	8120	1.35	5180
MAI 2	4500	5420	1.20	4724
MAI 3	4150	5130	1.24	4244

Synthesis of Macro-azo-initiator 2 (MAI 2)

MAI 2 was prepared from isocyanate-capped PEGMME(1) and ACPA in dioxane with the catalyst T-12, at room temperature, under dry nitrogen for 7 days. The resulting product, after evaporation of dioxane, was precipitated with petroleum ether and washed several times. After drying in a vacuum, MAI 2 was characterized with IR, GPC, and $^1\text{H-NMR}$ spectroscopy. The reaction scheme of MAI 2 is given in Scheme 2.

Synthesis of Macro-azo-initiator 3 (MAI 3)

The macro-azo-initiator (MAI 3) was synthesized from 4,4'-azobis(4-cyanopentanoyl chloride), ACPC, and PEGMME in benzene. ACPC was prepared according to the procedures outlined by Smith¹³ and Cowie and Pedram.¹⁴

ACPC was added gradually (in 30–40 min) into the benzene solution of PEGMME at 0–5°C. After 20 h stirring at room temperature, the product was obtained and precipitated from petroleum ether. The resulting product (MAI 3) was dried in a vacuum. The reaction of MAI 3 can be seen in Scheme 3.

Synthesis of Block Copolymers of Poly(dicyclohexylitaconate)-b-Poly(ethylene glycol), PDCHI-b-PEG

Macro-azo-initiators (MAIs) were used in the free-radical polymerization of dicyclohexylitaconate (DCHI) in bulk. As an example, block copolymerization to synthesize PDCHI-*b*-PEG was carried out as follows: MAI, 3 g, and DCHI, 7 g, were charged into a Pyrex tube. The tube was sealed by using a high vacuum line. Polymerization was carried out at 85°C for 85 h. The solid products were dissolved in benzene (in dioxane for copolymer with MAI 1) and precipitated in a large amount of methanol. They were filtered and dried *in vacuo* at 30°C for 48 h.

RESULTS AND DISCUSSION**Characterization of Macro-azo-initiators by IR, $^1\text{H-NMR}$, and GPC**

The synthesis and reaction scheme of MAIs were given in the Experimental section. Characterization of intermediates and final products were made by chemical analyses, IR, and $^1\text{H-NMR}$ and GPC techniques. Figure 1 shows the IR spectra of the initial materials, intermediates, and the product of MAI 1.

The unreacted —NCO content in MAI 1 was determined by end-group titration and found to be only 1.85%. The $^1\text{H-NMR}$ spectrum of MAI 1 is shown in Figure 2.

The preparation of MAI 2 was based on a capping reaction between isocyanate-capped PEGMME and ACPA. The proceedings of this reaction was followed by the disappearance of the characteristic peak of the —NCO stretching vibration at 2280 cm^{-1} in the IR spectrum. Figure 3 shows the presence of an urethane peak around 3440 cm^{-1} due to the —NH stretching in the —N—C=O group of this macroinitiator.¹⁵ Other characteristic peaks at 1720 cm^{-1} (carbonyl) and 1100–1110 cm^{-1} (etheric bond of PEG) are also present in this spectrum. Figure 4 shows the $^1\text{H-NMR}$

Table II DSC Results of MAIs

Macro-azo-initiator	ϕ (°C/min) ^a	T_p (°C) ^b	ΔE^c (kJ/mol)
MAI 1	2	109	107
	5	118	
	10	128	
	15	—	
	20	135	
MAI 2	2	—	110
	5	—	
	10	123	
	15	128	
	20	131	
MAI 3	2	—	108
	5	113	
	10	120	
	15	125	
	20	129	

^a ϕ = heating rate.

^b T_p = temperature at the maximum of the exotherm.

^c ΔE = activation energy.

NMR spectrum which confirms the structural formula of MAI 2.

The third approach for synthesis of the macro-azo-initiator (MAI 3) with PEG units, suitable for obtaining AB block copolymers, was the most conventional one, through the chloride of ACPA. In the literature, there exists two main procedures for ACPC preparation with SOCl_2 and PCl_5 .^{13,14,16} In this work, better results were obtained with PCl_5 . The melting point of the recrystallized product (ACPC) was 88–89°C. The reaction conditions for preparation of MAI 3 were given in the Experimental part. Figure 5 shows the characteristic peaks at 1750 cm^{-1} (carbonyl) and 1110 cm^{-1} (etheric bonds of PEG). The ^1H -NMR spectrum of MAI 3 is presented in Figure 6. GPC results of MAIs are given in Table I. A good correlation with the calculated values of molecular weights indicates that the reactions proceeded almost quantitatively.

Thermal Behaviour of MAIs

Table II summarizes the DSC results of MAIs. Each MAI showed an exothermic peak due to the decomposition of azo units in the molecule. T_p is the temperature at the maximum of the exotherm and ϕ shows the heating rates in $^\circ\text{C}/\text{min}$. Figure

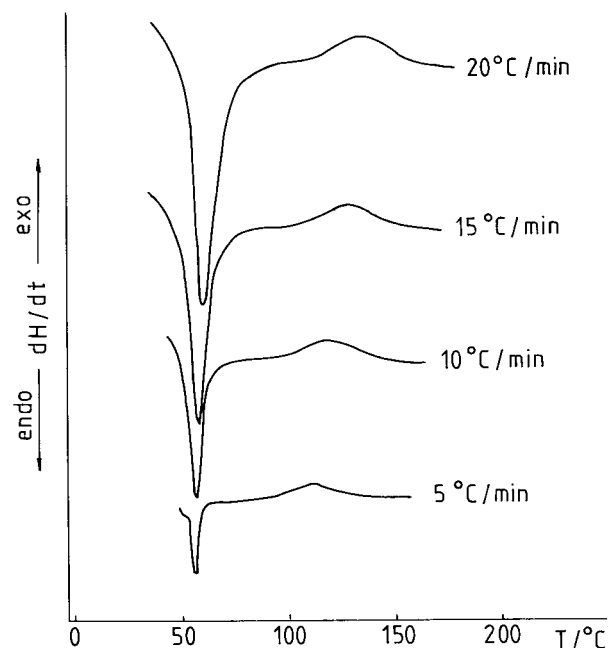


Figure 7 Typical DSC curves of MAI 3 under various heating rates.

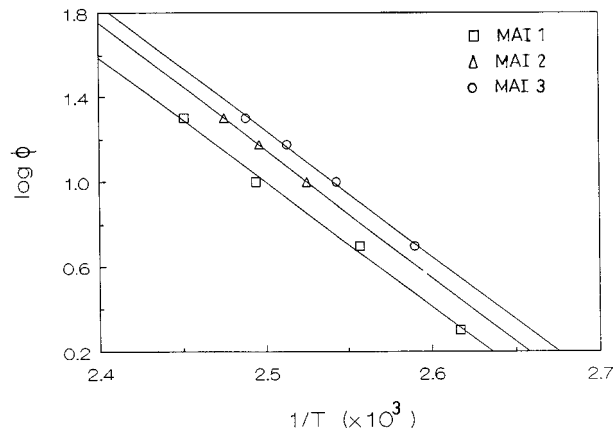


Figure 8 Typical relationships between reciprocals of decomposition temperatures ($1/T$) and logarithms of heating rate ($\log \phi$) for MAI 1, 2, and 3.

7 also shows the examples of DSC curves of MAI 3. The activation energies (ΔE) for MAIs were calculated as the slope of plotting $\log \phi$ vs. $1/T$ by using the following Ozawa relationship^{2,17}:

$$\log \phi = -0.4567\Delta E/RT + b \quad (1)$$

Figure 8 shows the typical relationships between the reciprocals of decomposition temperatures and the logarithms of heating rate (ϕ) for MAIs. Activation energies, ΔE (kJ/mol), of each

Table III Thermal Gravimetric Analysis Results of MAIs

T ($^\circ\text{C}$)	Weight Loss (%)		
	MAI 1	MAI 2	MAI 3
80	1.5	0.5	0.5
100	2.0	0.5	1.0
150	3.0	1.5	2.5
200	4.5	2.5	3.5
250	11	5.6	4.0
300	22	9.0	5.0
325	28	10	—
350	40	14	8.0
375	70	22	18
400	89	50	55
425	90	94	94
450	92	97	9.5
500	93	—	—
ΔE (kJ/mol)	133	159	136

The onset and final temperatures are 25 and 180°C, respectively. Range is 5 mV/cm, under N_2 atmosphere.

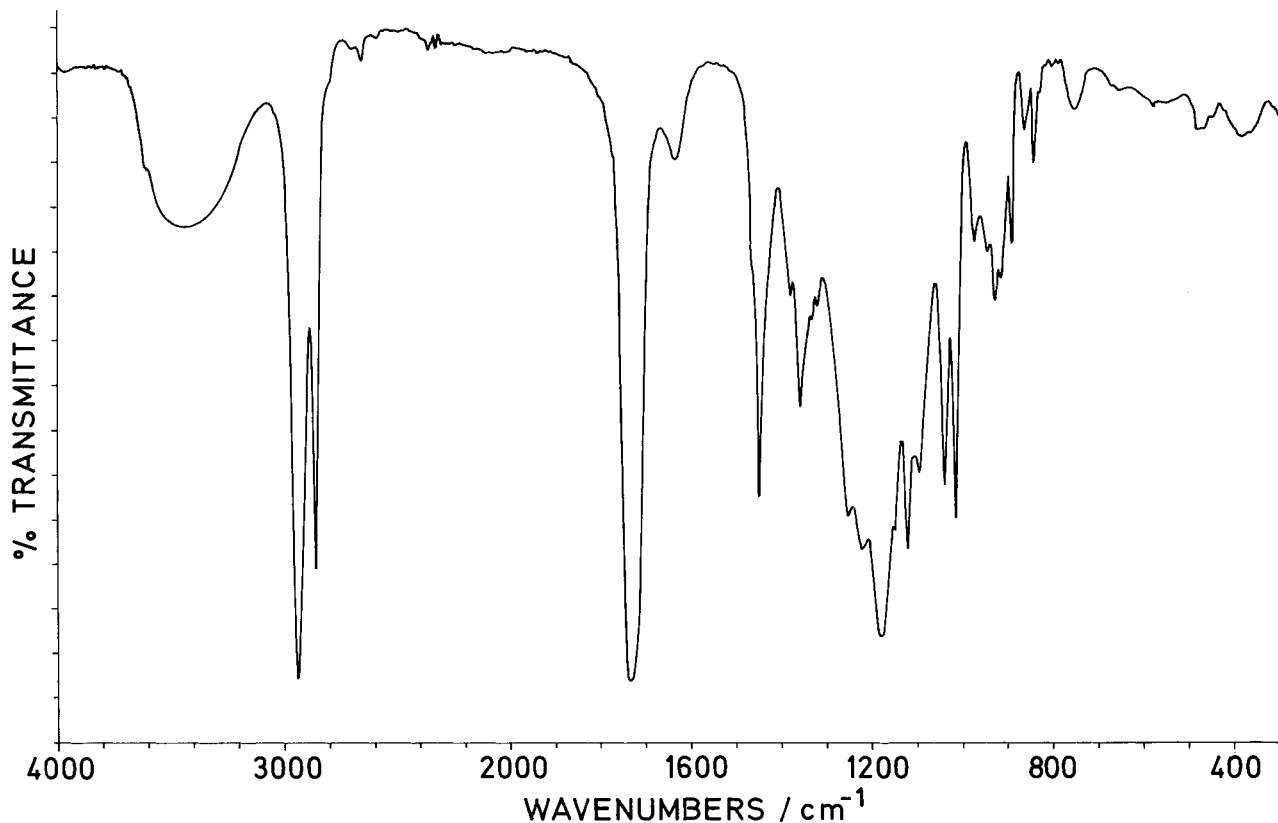


Figure 9 IR spectrum of PDCHI-*b*-PEG AB-type block copolymer (copolymer 3 in Table V).

MAI showed nearly the same value. Since the results are comparable with the data given in the literature for different types of polyester macro-azo-initiators,² it might be suggested that the thermal decomposition behavior of azo units in MAIs is independent of the structure of the prepolymer combined. The activation energy for ACPA crystal, determined by DSC, is 154.6 kJ/mol.² The lower ΔE values of MAIs from the pure ACPA value may be caused by the softening of PEG around the decomposition temperature and PEG may behave like a solvent to give a broader and lower decomposition peak.

Table IV GPC Results of PDCHI-*b*-PEG AB-type Block Copolymers

Copolymer	$M_n \times 10^{-3}$ (g/mol)	$M_w \times 10^{-3}$ (g/mol)	M_w/M_n
1	12.3	24.7	2.00
2	14.4	24.6	1.70
3	11.0	16.8	1.52

The thermal decomposition of MAIs was also studied by thermal gravimetric analysis (TGA). The approximate value of the activation energy was calculated using the relation given by Reich and Levi,^{18,19} as follows:

$$\ln |\ln(1 - c)| = -E/RT + \ln(A\Delta T/\beta) \quad (2)$$

where c is the conversion and defined by $c = 1 - (w/w_0)$ and w_0 and w represent the initial weight and weight any time, respectively. The apparent reaction order was assumed to be unity. In the TGA, the rate of heating $\beta = dT/dt$ is kept constant and ΔT is the temperature intervals for the reading of c . A represents the preexponential factor in the Arrhenius equation. Thermal gravimetric analysis results are summarized in Table III. Activation energies (ΔE) were calculated from the slope of the plot $\ln |\ln(1 - c)|$ vs. $1/T$. The activation energy values obtained by the TGA method seem to be higher than those obtained by DSC.

Synthesis and Characterization of Copolymers

Macro-azo-initiators having PEG units (MAI 1–3) were used in the synthesis of block copolymers of poly(dicyclohexylitaconate-*b*-ethylene glycol) (PDCHI-*b*-PEG). The resulting copolymers were characterized by IR and GPC analyses. Figure 9 shows the typical IR spectrum of the PDCHI-*b*-PEG copolymer (No. 3, prepared by MAI 3). In the IR spectra, the characteristic peaks at 1730 cm^{-1} for carbonyl ester groups, at 1450 cm^{-1} for $-\text{CH}_2$ groups of cyclohexyl units, and at 1100 cm^{-1} for etheric bonds of PEG were observed. GPC results of block copolymers are given in Table IV.

The observed two- or threefold increase in molecular weights indicates the formation of block copolymers. Detailed studies on the compositional tacticity determination of the AB-type PDCHI-*b*-PEG block copolymers and their use as additives in PDCHI/PEO blends are underway.

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