

Bulk Anionic Copolymerization of ϵ -Caprolactam in the Presence of Macroactivators Derived from Polypropylene Glycol

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SYNOPSIS

Bulk anionic copolymerization of ϵ -caprolactam (CPL) was conducted, under four different conditions by changing temperature (110 or 125°C) and [NCO]/[NaH] ratio (1, 2, or 3), in the presence of NCO-terminated polypropylene glycol (P1) and its CPL-blocked prepolymer (P2). Under the same conditions and reaction time, the conversion of CPL and reduced viscosity of the P2 system were higher than those of the P1 system. However, at the same conversion the P1 system showed higher viscosity for reactions at 125°C with [NCO]/[NaH] = 3 and at 110°C with [NCO]/[NaH] = 2. These results were attributed to cyclotrimerization of NCO groups of P1 (formation of isocyanurate) at the initial stage, which not only consumed the effective concentration of NCO but also increased the viscosity of the P1 system. Comparing IR spectra of the reaction products of model compounds, phenyl isocyanate and CPL-blocked phenyl isocyanate, with NaH/CPL also supported this conclusion. The crystalline melting temperature (T_m = 198–208°C) and melting enthalpy of the final products depended on the conversion of CPL and the types of macroactivators. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

During the last decades, several reports have been published on the synthesis of lactam-based block copolymers.^{1–7} Triblock copolymers, with an elastomeric central sequence and terminal blocks as cohesive as nylon-6, are, indeed, attractive materials. The high melting point of nylon-6 (220–230°C) can significantly improve the range of service temperature of the usual thermoplastic elastomers. On the other hand, block copolymers based on nylon might be considered in the solution of some problems of interfacial interaction between a polymeric material and nylon-reinforcing fibers. Finally, the presence of soft central blocks (like polypropylene glycol) in

nylon-6 should enhance its impact strength significantly.

The anionic polymerization of ϵ -caprolactam (CPL) has been extensively studied.⁸ It is well known that suitable cocatalysts or activators (isocyanates, acid chlorides, acid anhydrides, etc.) that form a *N*-acyl lactam entity *in situ* are needed to avoid the slow initiation observed when CPL is polymerized by strong bases.^{9–11} Furthermore, the activator residues are incorporated at the end of the resulted nylon-6. Accordingly, every polymer chain capped, at both ends, with one of the activators mentioned could be potentially used for the synthesis of triblock copolymers.

We report here the results of applying NCO-terminated polypropylene glycol (P1) and its CPL-blocked prepolymer (P2), separately, as macroactivators in CPL anionic polymerization for the preparation of nylon-6-PPG-nylon-6 triblock copolymers. The difference in polymerization behaviors are discussed in terms of reaction conditions and side reactions of NCO at the initial stage.

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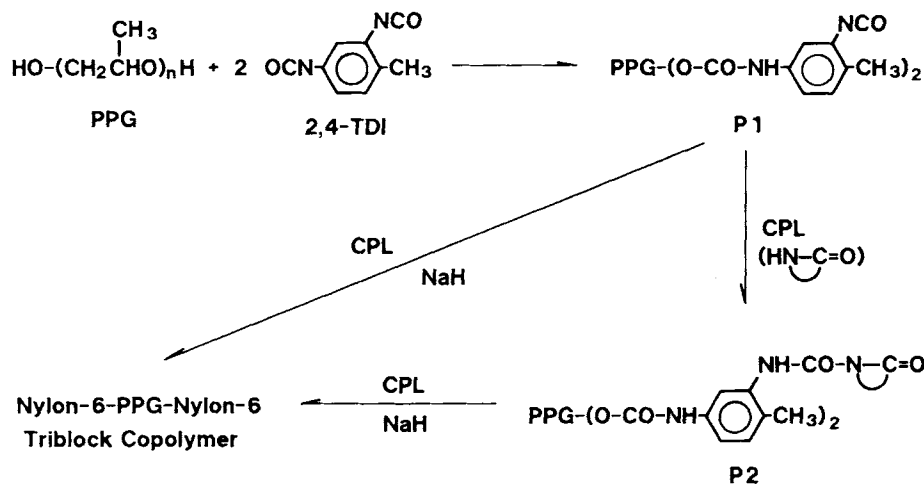
EXPERIMENTAL

Materials

Polypropylene glycol (PPG-3000), supplied by Cheng-Lung Co., has the following properties: $M_n = 3000$; hydroxyl value = 38 ± 3 ; acid value = 0.1% max; and viscosity = 500 cps at 25°C. It was vacuum-dried at 115°C for 2 days before use. Toluene-2,4-diisocyanate (Wako) was distilled at 102°C/5 mmHg before reaction. ϵ -Caprolactam was pure re-

agent and recrystallized twice in cyclohexane and dried *in vacuo* for 24 h. Before polymerization, CPL was purged with nitrogen at 100°C until the water content was less than 100 ppm, determined by a Karl Fisher Moisture Meter of Kyoto Electronic Co., Model MKA-3. Sodium hydride (Wako) was used as a 60% dispersion in paraffin oil. Acetone, *m*-cresol, and di-*n*-butylamine were pure reagents and used as received.

Synthesis of NCO-Terminated PPG-3000 (P1) (Scheme 1)



To a previously flamed, nitrogen-purged 500 mL flask were added 300 g of PPG-3000 (0.10 mol) and 35.4 g of toluene-2,4-diisocyanate (TDI; 2.03 mol). The mixtures were allowed to react at 80°C until the theoretical NCO% (2.55%) was approached. After reacting for 6 h, the NCO content was 2.57%, as determined by a di-*n*-butylamine titration method.¹²

Synthesis of CPL-Blocked Prepolymer (P2) (Scheme 1)

Thus-obtained NCO-terminated PPG-3000 (150 g) was then allowed to react with an excess of ϵ -caprolactam (20.8 g; [CPL]/[NCO] = 2) at 95°C. The progress of the blocking reaction was followed by infrared spectra until the disappearance of NCO absorption at 2270 cm^{-1} . It took about 2 h to complete the reaction. The model compound from phenyl isocyanate and CPL was synthesized by similar procedures except that the [CPL]/[NCO] ratio was 1.2.

Bulk Anionic Copolymerization of CPL

To a clean, nitrogen-purged 100 mL flask containing a magnetic stir bar was added 64 g of CPL (or 61.8

g for P2 system). The content was heated to 100°C and then purged with nitrogen until the water content was less than 100 ppm. Suitable amounts of NaH were added and the nitrogen-purging was continued for another 10 min to remove the hydrogen gas produced. The melts were injected into a flask that contained 16 g of P1 (or 18.2 g of P2) and had been heated to 100°C under vigorous stirring. The mixtures were injected into six to eight vials (10 mL each) under a nitrogen blanket, and the vials were immediately sealed and put into an oil bath maintained at constant temperature. After predetermined times, the vials were successively taken out and quenched in ice water, and the solid polymers were isolated by breaking the vials. The CPL content was kept at 80 wt % for all experiments and the reaction temperature was 110 or 125°C. The ratio of macroactivator chain-end (NCO in P1 or CPL-blocked NCO in P2) to NaH was adjusted to 1–3 and expressed as [NCO]/[NaH] throughout the text (see Tables I–IV).

Analysis

The conversion of CPL was evaluated by extraction of the isolated polymers with distilled water. This

Table I Bulk Anionic Polymerization of CPL at 125°C with [NCO]/[NaH] = 3 in the Presence of P1 and P2^a

Polymerization Time (Min)	Conversion of CPL (%)	Block Copolymer		Extracted Prepolymer (%)
		η_{red}^b	CPL (wt %) ^c	
30	25.7	0.83	53.6	10.95
	(31.6)	(1.01)	(58.4)	(10.13)
60	43.0	1.79	64.9	6.92
	(48.8)	(2.46)	(67.6)	(6.52)
90	51.5	3.20	68.8	6.41
	(56.5)	(3.55)	(71.0)	(7.65)
130	57.9	4.03	71.0	5.47
	(60.8)	(4.22)	(72.1)	(6.10)
180	63.0	4.50	72.7	5.87
	(66.4)	(4.61)	(73.8)	(5.89)
240	68.2	4.59	74.1	4.61
	(70.8)	(4.87)	(74.9)	(5.29)
300	72.6	4.58	75.3	4.91
	(74.3)	(4.79)	(75.7)	(4.65)
360	75.1	4.53	75.9	4.65
	(78.0)	(4.68)	(76.8)	(5.53)

^a Values in parentheses are those of the P2 system.

^b Reduced viscosity: measured at 30°C with a concentration of 0.5 g/dL *m*-cresol using an Ubbelohde viscometer.

^c After extraction with water and acetone.

was accomplished by stirring 5 g of the pulverized polymers with 200 mL of water at 65°C until constant weight was reached. The conversion of CPL (%) was estimated by $100 \times [0.8W_1 - (W_1 - W_2)] / 0.8W_1$, where W_1 and W_2 were the weight of sample before and after extraction, respectively. The content of unreacted macroactivator was estimated by further extraction with 160 mL of acetone at 50°C for 4 days. The extracted prepolymer (%) was es-

timated by $100 \times (W_2 - W_3) / 0.2W_1$ [or $100 \times (W_2 - W_3) / 0.228W_1$ for the P2-system], where W_3 was the weight after extraction with water and acetone. Reduced viscosity ($\eta_{red} = \eta_{sp}/C$) was determined in 0.5 g/dL *m*-cresol at 30°C using an Ubbelohde viscometer.

Infrared spectra (IR) were recorded using an IR spectrophotometer, Perkin-Elmer, Model 710B, equipped with a heating cell, at a resolution of 4

Table II Bulk Anionic Polymerization of CPL at 110°C with [NCO]/[NaH] = 2 in the Presence of P1 and P2^a

Polymerization Time (Min)	Conversion of CPL (%)	Block Copolymer		Extracted Prepolymer (%)
		η_{red}	CPL (wt %)	
40	24.9	0.86	52.2	8.85
	(26.0)	(0.88)	(53.6)	(9.85)
80	41.4	1.32	64.1	7.24
	(46.4)	(1.44)	(66.5)	(6.38)
130	55.3	1.89	70.1	5.71
	(62.1)	(1.92)	(72.5)	(6.03)
200	67.1	2.16	73.5	3.11
	(72.7)	(2.44)	(74.9)	(2.40)
290	77.6	2.77	76.0	1.84
	(83.1)	(2.86)	(77.1)	(1.05)
410	83.6	2.98	77.1	0.47
	(89.7)	(3.14)	(78.3)	(0.65)

^a Values in parentheses are those of the P2 system.

Table III Bulk Anionic Polymerization of CPL at 110°C with [NCO]/[NaH] = 1 in the Presence of P1 and P2^a

Polymerization Time (Min)	Conversion of CPL (%)	Block Copolymer		Extracted Prepolymer (%)
		η_{red}	CPL (wt %)	
20	62.0 (71.8)	1.71 (2.83)	74.3 (77.1)	14.27 (14.49)
40	93.1 (94.2)	3.74 (4.58)	81.2 (81.4)	13.98 (13.89)
60	93.8 (94.2)	3.78 (5.01)	81.2 (81.6)	13.27 (14.90)
90	94.7 (95.1)	4.35 (5.47)	81.3 (81.7)	13.09 (14.54)
130	95.4 (95.6)	4.16 (4.85)	81.5 (81.8)	13.49 (15.20)
190	95.7 (96.8)	3.75 (4.12)	81.7 (81.9)	14.09 (14.36)

^a Values in parentheses are those of the P2 system.

cm⁻¹. A differential scanning calorimeter of Perkin-Elmer, Model DSC-2, was used to detect thermal transitions of the block copolymers between 50 and 250°C. The sample was 4 mg and the heating rate was 20°C/min under nitrogen.

RESULTS AND DISCUSSION

Unblocking Behavior of CPL-Blocked Prepolymer (P2)

To investigate side reactions of NCO-terminated PPG-3000 (P1), its CPL-blocked prepolymer was

also prepared for comparison. However, it is well known that CPL-blocked isocyanate unblocks (dissociates to NCO and CPL) at elevated temperature. To ascertain the blocked state of P2 during polymerization, it was heated to 100–175°C, temperatures at which its IR spectra were recorded. As shown in Figure 1, at 100°C, no characteristic absorption of isocyanate at 2270 cm⁻¹ could be observed. At 115°C, which was within the range employed for polymerization (110–125°C), a small IR absorption appears. However, the intensity is much less than that of P1, indicating that the unblocking of CPL-blocked isocyanate in P2 can be neglected in this temperature range.

Table IV Bulk Anionic Polymerization of CPL at 125°C with [NCO]/[NaH] = 1 in the Presence of P1 and P2^a

Polymerization Time (Min)	Conversion of CPL (%)	Block Copolymer		Extracted Prepolymer (%)
		η_{red}	CPL (wt %)	
15	90.8	—	52.2	19.08
(12)	(87.3)	(—)	(53.6)	(19.66)
30	94.9	—	64.1	23.42
(24)	(95.4)	(—)	(66.5)	(22.95)
45	95.2	Gels	70.1	24.03
(37)	(95.7)	(Gels)	(72.5)	(26.50)
65	95.5	Gels	73.5	23.45
(57)	(96.0)	(Gels)	(74.9)	(27.22)
95	96.3	Gels	76.0	25.80
(87)	(96.4)	(Gels)	(77.1)	(27.43)
135	96.3	Gels	77.1	24.13
(127)	(96.4)	(Gels)	(78.3)	(25.24)

^a Values in parentheses are those of the P2 system.

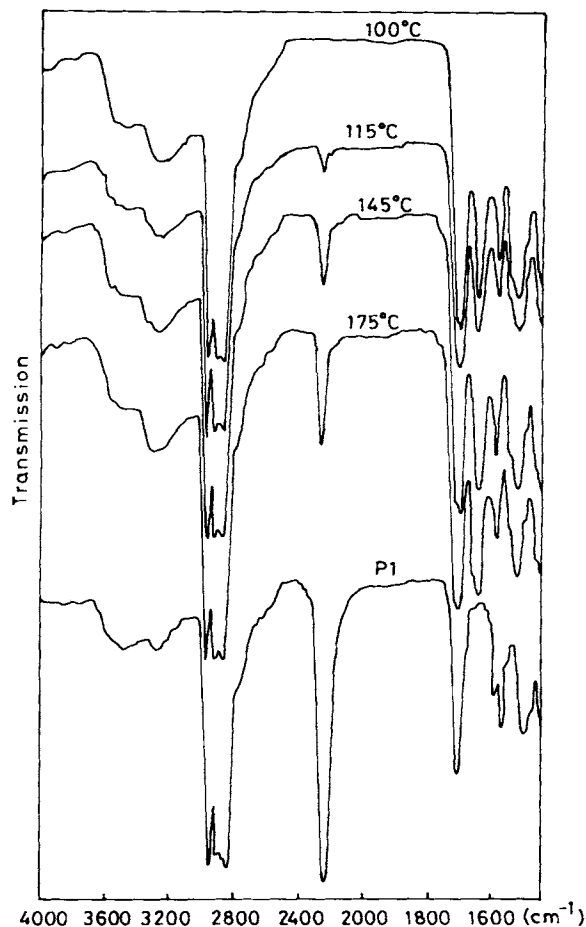


Figure 1 IR spectra of CPL-blocked prepolymer (P2) at different temperatures. $[\text{CPL}]/[\text{NCO}] = 2$.

Bulk Anionic Copolymerization of CPL

The bulk anionic polymerization of CPL in the presence of macroactivators P1 and P2 was carried out, separately, under four different conditions (Tables I–IV). For both systems, the clear reaction mixtures became translucent (solidification) after reacting for 10–40 min, depending on reaction temperature and $[\text{NCO}]/[\text{NaH}]$ ratio. The concentration of CPL was kept at 80 wt % for all systems, i.e., in case of P2, it included the CPL that had been bonded to P1. The polymerization behaviors are discussed as follows:

Polymerization at 125°C with $[\text{NCO}]/[\text{NaH}] = 3$

Table I and Figures 2 and 3 show the changes of CPL conversion, reduced viscosity, and extracted prepolymer (%) with reaction time. For both systems, the conversion increases smoothly with time. However, the conversions in the P2 system are higher than those in P1 system, in which the dif-

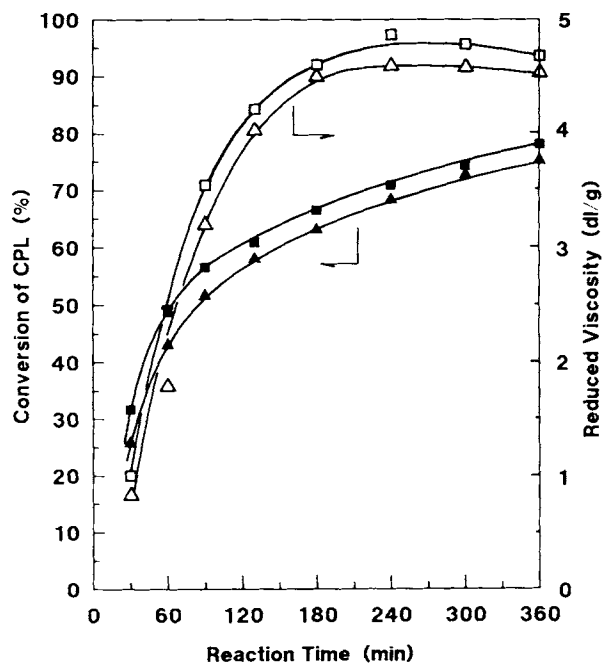


Figure 2 The change of conversion and reduced viscosity with reaction time. Polymerized at 125°C with $[\text{NCO}]/[\text{NaH}] = 3$ in the presence of ($\blacktriangle, \triangle$) P1 or (\blacksquare, \square) P2.

ference is 5.9% at 30 min. These results suggest that, in the P1 system side reactions should occur during the initial stage, because the calculated conversion difference of CPL between P1 and P2 is only 3.44%

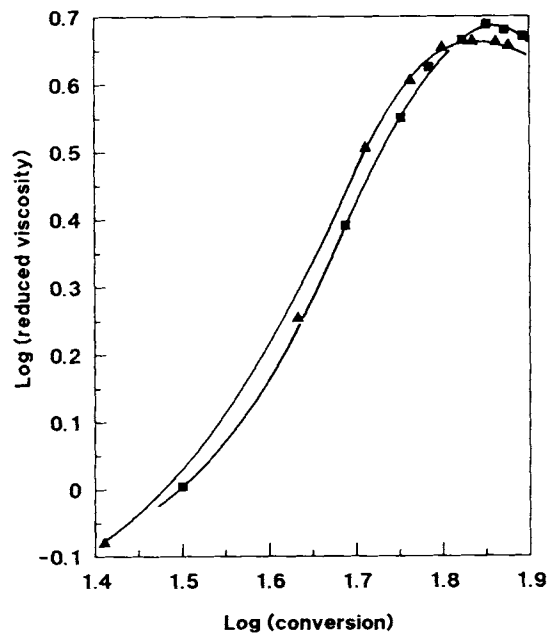


Figure 3 Log(reduced viscosity) vs. log(conversion). Polymerized at 125°C with $[\text{NCO}]/[\text{NaH}] = 3$ in the presence of (\blacktriangle) P1 or (\blacksquare) P2.

if the bonded CPL in P2 is taken into account. Reduced viscosity appears to increase with time for the first 4 h and then decreases slightly (Fig. 2). The viscosity depression during later stages would be caused by the chain scission of amide linkage by reactive CPL anions.⁸

Furthermore, from the S-shaped curves in $\log(\eta_{red})$ vs. $\log(\text{conversion})$ plots, as shown in Figure 3, the polymerization clearly is not a living process.¹ The quick viscosity increase with conversion can be explained by the branching side reactions.⁸ It is interesting to note that, at the same conversion, the P1 system shows higher viscosity than does the P2 system, except in later stages. This can also be attributed to the initial side reaction of isocyanate in P1 (see Side Reactions section).

The percentage of extracted prepolymer is an effective quantity in evaluating the initiation efficiency of the macroactivators.³ As described in Table I, for both macroactivators, the percentage of extracted prepolymers decrease from ca. 10% to 5% as the polymerization proceeds. This result indicates that the initiation is not instantaneous due to limited compatibility of PPG with CPL and nylon-6, and chain ends of the macroactivators must diffuse out from PPG domain before they have a chance to react with CPL anions.

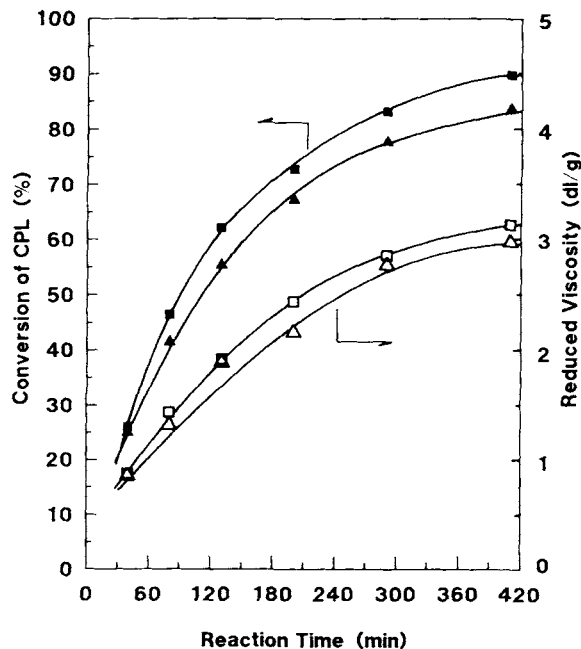


Figure 4 The change of conversion and reduced viscosity with reaction time. Polymerized at 110°C with $[\text{NCO}]/[\text{NaH}] = 2$ in the presence of ($\blacktriangle, \triangle$) P1 or (\blacksquare, \square) P2.

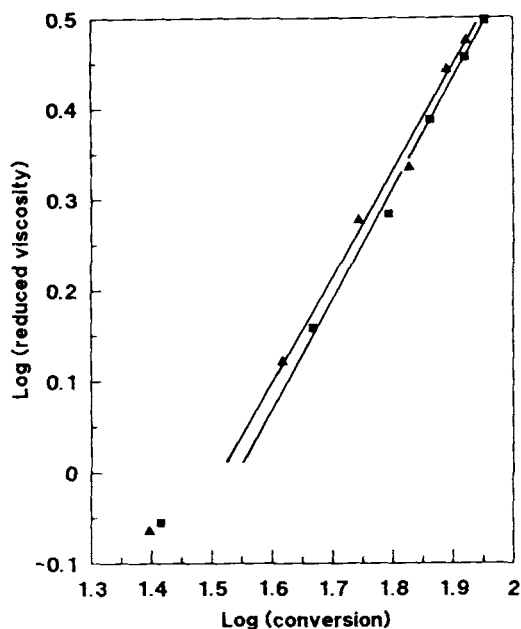


Figure 5 $\log(\text{reduced viscosity})$ vs. $\log(\text{conversion})$. Polymerized at 110°C with $[\text{NCO}]/[\text{NaH}] = 2$ in the presence of (\blacktriangle) P1 or (\blacksquare) P2.

Polymerization at 110°C with $[\text{NCO}]/[\text{NaH}] = 2$

The results are shown in Table II and Figures 4 and 5. Similar trends in conversion, reduced viscosity, and extracted prepolymer with reaction time are obtained in these milder conditions. However, comparing with those polymerized at 125°C with $[\text{NCO}]/[\text{NaH}] = 3$, the plot of $\log(\eta_{red})$ vs. $\log(\text{conversion})$ is approximately linear, except at the initial stage, suggesting that the polymerization is a living one.¹ In addition, the extracted prepolymer decreases harmoniously from ca. 9 to 0.5% as the polymerization proceeds. This means that although the initiation process is not an instantaneous one, the initiation efficiency increases with reaction time and can reach as high as 99.5%.

Polymerization at 110°C with $[\text{NCO}]/[\text{NaH}] = 1$

By increasing NaH concentration to $[\text{NCO}]/[\text{NaH}] = 1$, the initial concentration of the CPL anion is equal to that of chain ends of the macroactivators. The results are shown in Table III and Figures 6 and 7. The conversion appears to be higher than 90% after reacting for 40 min and remains almost unchanged throughout the rest of the reaction. The reduced viscosity at first rises quickly and then falls smoothly. These results indicate that increasing the CPL anion concentration not only enhances polymerization rate, but also increases the probability

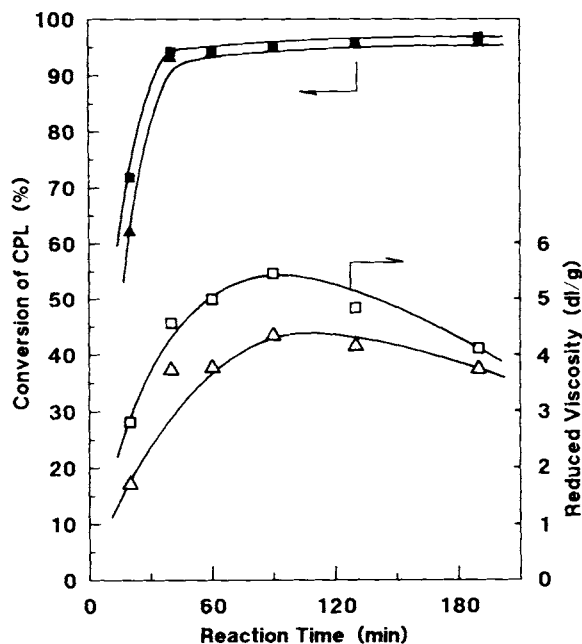


Figure 6 The change of conversion and reduced viscosity with reaction time. Polymerized at 110°C with $[\text{NCO}]/[\text{NaH}] = 1$ in the presence of ($\blacktriangle, \triangle$) P1 or (\blacksquare, \square) P2.

of chain scission by reactive CPL anions. The conversion and viscosity of the P2 system are higher than those of the P1 system, which are similar to the foregoing two conditions. However, in contrast to the results obtained above, the P2 system shows greater viscosity than does the P1 system at the same conversion (Fig. 7). It is presumably caused by the

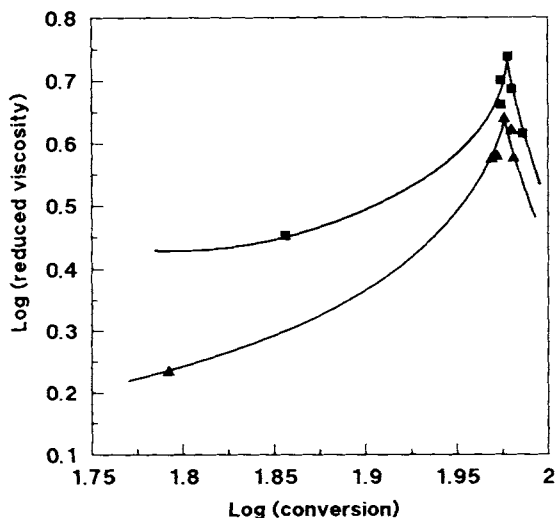


Figure 7 $\text{Log}(\text{reduced viscosity})$ vs. $\text{log}(\text{conversion})$. Polymerized at 110°C with $[\text{NCO}]/[\text{NaH}] = 1$ in the presence of (\blacktriangle) P1 or (\blacksquare) P2.

intensive branching reaction that outweighs the influence of initial NCO side reaction. The $\text{log}(\eta_{\text{red}})$ vs. $\text{log}(\text{conversion})$ plots show sharp peaks near $\text{log}(\text{conversion}) = 1.97$ (95% conversion) for both systems. These interesting phenomena are not currently understandable, but could result from excessive chain scission reaction at this point.

The extracted prepolymers of these two systems are ca. 14% and remain almost constant throughout the polymerization (Table III), which are higher than those discussed above. This result clearly indicates that fast reaction (quick solidification) prevents chain ends of the macroactivators from diffusing out of the PPG domain.

Polymerization at 125°C with $[\text{NCO}]/[\text{NaH}] = 1$

Further increase in reaction temperature to 125°C at $[\text{NCO}]/[\text{NaH}] = 1$ results in very fast reaction and gel formation, as shown in Figure 8 and Table IV. The conversion reaches 90% after reacting for 15 min and increases very slowly with reaction time. After ca. 40 min, the samples cannot be completely dissolved in *m*-cresol, i.e., partial gels are formed. Accordingly, extensive branching reaction under this vigorous reaction condition results in the formation of partially cross-linked nylon-6. The percentages of extracted prepolymer are between 20% and 27%, which are the highest of the systems studied. Therefore, it is concluded that the more vigorous the reaction the lower the initiation efficiency.

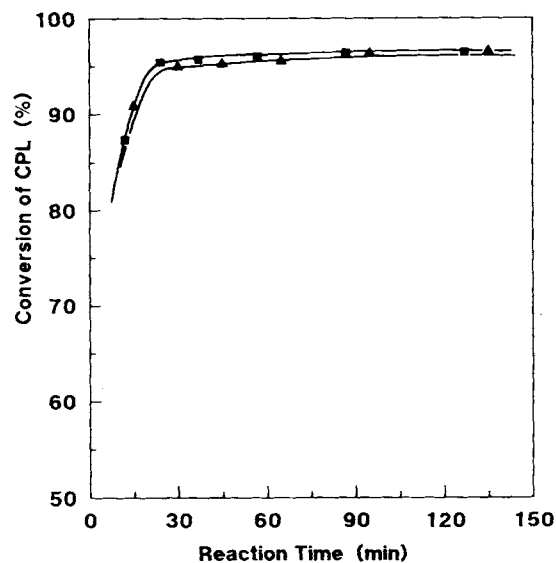


Figure 8 The change of conversion with reaction time. Polymerized at 125°C with $[\text{NCO}]/[\text{NaH}] = 1$ in the presence of (\blacktriangle) P1 or (\blacksquare) P2.

The final products of the above-mentioned reactions were homogeneous under an optical microscope ($\times 400$) and showed good mechanical strength. However, their electron photomicrographs ($\times 10,000$) exhibited continuous phases of nylon-6 with dispersed domains of PPG. It is concluded that the limited compatibility of the macroactivators with CPL and nylon-6 results only in microphase separation, not in macrophase separation. Therefore, this process can be applied to direct preparation of nylon-6-PPG-nylon-6 triblock copolymers by modifying the reaction conditions.

Side Reactions at the Initial Stage

From the foregoing results, the initial side reactions of isocyanate clearly are responsible for the higher viscosity of the P1 system at the same conversion. In a separate experiment at 100°C , NCO-terminated PPG-3000 gelled instantly on addition of a few drops of NaH/CPL solution. This also ascertains the existence of side reactions of NCO in the presence of CPL anions. However, the side reactions of NCO under basic conditions can be cyclotrimerization, formation of nylon-1, or formation of carbodiimide.⁶ To elucidate the true contributing side reaction, IR spectra of the reaction products of CPL-blocked phenyl isocyanate with NaH were compared with

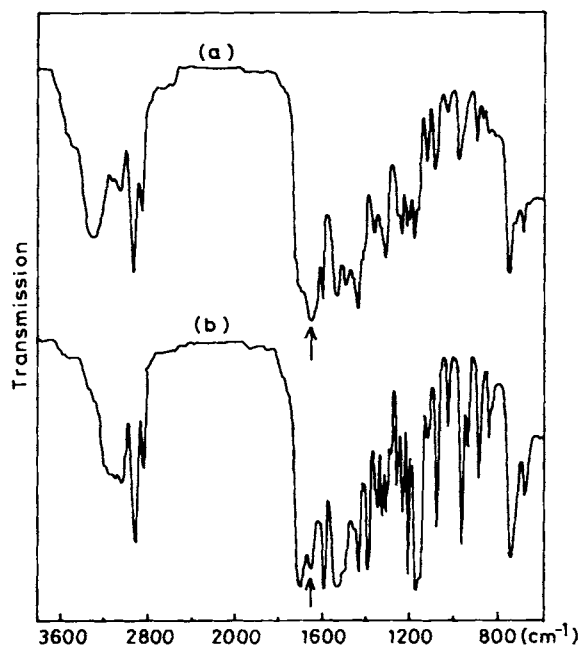


Figure 9 IR spectra of the reaction products of (a) phenyl isocyanate with CPL/NaH and (b) CPL-blocked phenyl isocyanate with NaH. $[\text{CPL}]/[\text{NCO}] = 1.2$, $[\text{NCO}]/[\text{NaH}] = 10$, and reacted at 100°C for 10 min.

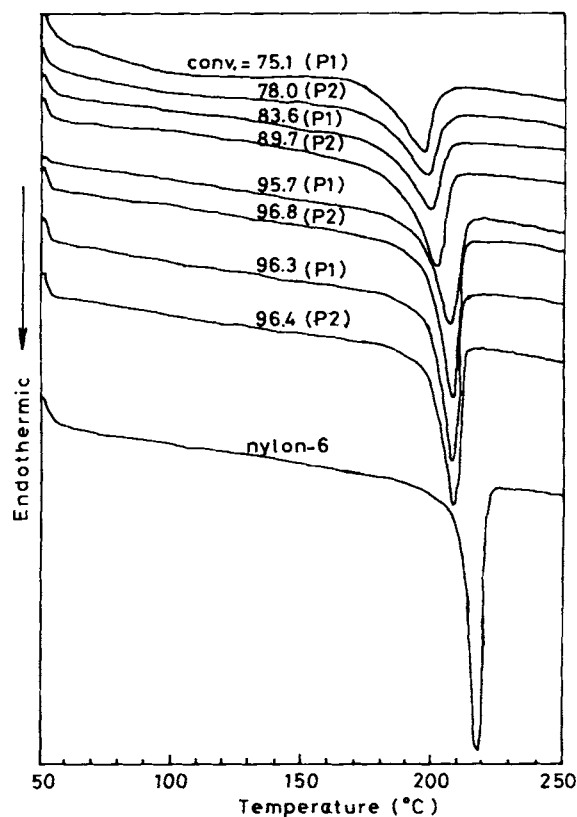


Figure 10 DSC curves of nylon-6-PPG-nylon-6 triblock copolymers and nylon-6 homopolymer. Heating rate: $20^\circ\text{C}/\text{min}$; sample weight: 4 mg.

those of phenyl isocyanate with NaH/CPL ($[\text{CPL}]/[\text{NCO}] = 1.2$ and $[\text{NCO}]/[\text{NaH}] = 10$). As shown in Figure 9, the reaction products of phenyl isocyanate with NaH/CPL show a stronger characteristic IR absorption of isocyanurate and nylon-1 at $1640\text{--}1700\text{ cm}^{-1}$ than those of CPL-blocked phenyl isocyanate. From this result and the absence of carbodiimide absorption at 2100 cm^{-1} ,¹² it is clear that the side reactions are mainly cyclotrimerization and/or formation of nylon-1. However, from the steric hindrance of *o*-methyl groups in toluene isocyanate units and high reaction temperature ($110\text{--}125^\circ\text{C}$), the nylon-1 formed is not stable.¹³⁻¹⁵ Accordingly, it is concluded that the main side reaction of P1, at the initial stage, is cyclotrimerization, i.e., formation of isocyanurate.

Thermal Behaviors of Nylon-6-PPG-Nylon-6 Block Copolymers

Differential scanning calorimetry (DSC) curves were obtained on the final triblock copolymers. Figure 10 shows their DSC curves compared with that

of nylon-6 homopolymer, which was prepared by CPL anionic polymerization in the presence of TDI. Both crystalline melting point T_m and melting enthalpy (ΔH_m) increase with conversion. The T_m and ΔH_m of copolymers from P2 are slightly higher than those from P1. This can be attributed not only to a difference in conversion, but also to the branching side reaction (cyclotrimerization) of NCO in P1. The T_m at 98% conversion is ca. 208°C, which is near the value of nylon-6 homopolymer (220°C).

CONCLUSIONS

We have investigated bulk anionic copolymerization of ϵ -caprolactam (CPL) in the presence of NCO-terminated PPG-3000 (P1) and its CPL-blocked prepolymer (P2) under four different conditions. It was found that, for both macroactivators, the conversion and viscosity increase with reaction time. The viscosities of the P2 system are higher than those of the P1 system at the same reaction time. However, at the same conversion, the relationship is reversed (for reaction at 125°C with $[\text{NCO}]/[\text{NaH}] = 3$ and at 110°C with $[\text{NCO}]/[\text{NaH}] = 2$). These results have been attributed to the cyclotrimerization side reaction of NCO groups of P1, which is also supported by IR analysis of the reaction products of the model compound. The initiation is not an instantaneous process due to limited compatibility of the macroactivators with CPL and nylon-6. The initiation efficiency increases with reaction when $[\text{NCO}]/[\text{NaH}]$ is 2 or 3, whereas at $[\text{NCO}]/[\text{NaH}] = 1$, it remains almost unchanged as polymerization proceeds. The final triblock copolymers are homogeneous under the microscope

and show melting points between 198 and 208°C, depending on the conversion of CPL and the types of macroactivators.

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