Segmented Block Copolyetheramides Based on Nylon 6 and Polyoxypropylene. I. Synthesis and Characterization

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SYNOPSIS

Various segmented block copolyetheramides based on nylon 6 and polyoxypropylene (POP) were synthesized by melt polymerization of caprolactam (CPL) and polyoxypropylene diamines (POPD) as a function of the size and content of POPD. As the content of POPD in the feed increased, the IR absorption band at 1110 cm^{-1} increased. The ^{1}H-NMR analysis indicated that peaks characteristic of methylene groups in POP unit appeared at 1.2, 3.6, and 3.8 ppm. The compositions of the hard and soft segments in the block copolymer were determined from the NMR data. The POP content in copolymer was higher than that in the feed due to the removal of unreacted CPL by water extraction. The average block lengths of the hard and soft segments were calculated from molecular weights and copolymer compositions. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Segmented block copolymers are of much interest as a thermoplastic elastomer (TPE) because most of them possess good solvent resistance, good mechanical properties, and wide application temperature ranges. If a segmented block copolymer consists of the soft and hard segments, it will act as a TPE. The polyethers such as polyoxypropylene (POP) or polytetramethylene oxide (PTMO) and aliphatic polyesters are often chosen as the soft segments in order to impart elastomeric properties to the polymer. The hard segments are usually composed of crystallizable units having a high melting temperature, thereby forming physical crosslinks that provide for dimensional stability and minimize cold flow. As these hard segments, the polyurethanes, polyesters, and polyamides have been of most interest.[1-3]

Among these segmented block copolymers the thermoplastic polyamide elastomers combine good mechanical properties with a good performance at low temperatures. But investigations of this block copolymer as a TPE were relatively few compared

to others. Segmented block copolyetheramides have been synthesized by several different chemical approaches, resulting in amide,[4-6] urethane,[7] urea,[8] or ester[9-13] linkages between poloyether and polyamide segments. The third linkage groups, besides the amide or ether group, in copolyetheramide may induce more complex aspects in microstructure and properties of the polymer. Accordingly, the use of the amine- or acid-terminated polyether is more desirable in order to avoid the introduction of this third group. At the present time, a systematic study on segmented block copolyamides has not been reported as a function of block lengths of the hard and soft segments.

In this study segmented block copolyetheramides based on nylon 6 and POP without the third linkage group were synthesized varying the contents and block lengths of the POP unit, and their composition and block lengths are quantitatively determined.

EXPERIMENTAL

Materials

The commercial fiber-grade caprolactam (CPL) from BASF and three grades of polyoxypropylene diamine (Jeffamine D-400, D-2000, and D-4000) from Texaco Chemical Co. were used as received.

Adipic acid (ADA) as an extra pure grade of Shinyo Chemical Co. was used without further purification. All materials used for polymerization are listed in Table I.

Polymerization

A stoichiometric amount of ADA and polyoxypropylene diamine (POPD) was added to CPL in order to avoid limiting the degree of polymerization. The 2 wt % of distilled water for CPL was used as a ring-opening catalyst. The polymerization was carried out in a 2-L autoclave equipped with anchor stirrer and electric heater, which is carefully designed for preventing the degradation of polymer due to overheating. The synthesis of block copolymers was carried out in two steps: in the first step the ring-opening reaction of CPL was conducted under the pressure of 3–5 kg/cm^2 and the second step was performed to increase the molecular weight under vacuum of 300 mmHg. All materials were poured together into the autoclave and heated to 240°C for about 90 min, when the pressure of the autoclave was increased up to 5 kg/cm^2. After 3 h the pressure was released and reduced to 300 mmHg by vacuum pump over 1 h. The polymerization was carried out at 240°C for the desired time. The product was washed with the distilled water by Soxhlet apparatus for 30 h in order to remove sufficiently the unreacted monomers or oligomers and dried in a convection oven at 75°C for 48 h. The yields were calculated from the weight reduction after extraction.

Characterization

End Group Analysis

The amine end groups were measured by potentiometric titration of a 100-mg sample in 50 mL phenol at 80°C with 0.01N perchloric acid in methanol. The concentration of carboxylic acid end groups of a 200-mg sample dissolved in 20 mL benzyl alcohol was

determined by a titration method with 0.02N KOH in methanol using phenolphthalein as an indicator.

Solution Viscosity

The relative viscosity of 1 g/dL polymer solution in 95% H$_2$SO$_4$ was measured by using Ubbelohde capillary viscometer in a constant-temperature water bath kept at 25°C.

IR Spectroscopy

Infrared (IR) absorption spectrum was obtained by use of a Bruker IFS 88 FT-IR spectrophotometer. The specimen in film form was prepared by melt-casting on a slide glass or KBr pellet.

NMR Spectroscopy

The sample was dissolved in HCOOH/CDCl$_3$ (3/2 v/v). ^{1}H-NMR spectroscopy was performed by using a JEOL JNM-EX400 FT-NMR (400 MHz) spectroscopy at room temperature. Tetramethylsilane (TMS) was used as an internal standard.

RESULTS AND DISCUSSION

Segmented block copolyetheramides were synthesized by a melt polymerization of CPL and POPD. The stoichiometry of the amine and acid groups was balanced by adding ADA. In order to obtain high-molecular-weight polymer, it is important to adjust exactly the stoichiometric balance of the acid and amine groups. Generally, this stoichiometric balance in the synthesis of polyamides can easily be obtained by using the salt prepared from the diamines and diacids. However, it was difficult to control the stoichiometric balance in this system because it was not easy to purify the gel-like salt from POPD and ADA.

Polymerization conditions are listed in Table II. The numbers behind sample code D in Table II denote the species and content of POPD, e.g., D4-20

Table I List of Materials for Polymerization

Name	Abbr.	Chemical Structure	Specification	Source
Caprolactam	CPL	CO(CH$_2$)$_5$NH	mp. 69.2°C	BASF
Polyoxypropylene diamine	POPD	H$_2$NCHCH$_2$(OCH$_2$CH)$_n$NH$_2$		Texaco Chem. Co.
D-400	D-4	CH$_3$ CH$_3$	n = 6.7 (M_w 462)	
D-2000	D-20		n = 35 (M_w 2104)	
D-4000	D-40		n = 77 (M_w 4540)	
Adipic acid	ADA	HOOC(CH$_2$)$_4$COOH	mp. 153°C	Shinyo Pure Chem. Co.

Table II   Polymerization Conditions of Copolymers

Sample Code	CPL/POPD Feed Ratio	Melt Polymerization	Yield (%)
N-6	100/0	240°C, 7 h	88.5
D4-10	100/10	240°C, 9 h	90.2
D4-20	100/20	240°C, 9 h	90.5
D4-40	100/40	240°C, 9 h	91.5
D4-60	100/60	240°C, 9 h	91.6
D4-80	100/80	240°C, 9 h	93.6
D20-10	100/10	240°C, 8 h	85.6
D20-20	100/20	240°C, 8 h	90.7
D20-40	100/40	240°C, 8 h	90.8
D20-60	100/60	240°C, 8 h	91.2
D20-80	100/80	240°C, 8 h	92.5
D40-10	100/10	240°C, 5 h	89.3
D40-20	100/20	240°C, 5 h	91.4
D40-40	100/40	240°C, 5 h	91.5
D40-60	100/60	240°C, 5 h	91.5
D40-80	100/60	240°C, 5 h	93.4

indicates that 20 wt % of D-400 is used as a soft segment. The same temperature is applied for all samples, but the polymerization time is decreased with the increase of molecular weight of POPD. This is attributed to the fact that as the molecular weight of POPD becomes higher, the viscosity of polymer melt increases, giving rise to some troubles in discharge of the polymer melt from the reactor after the completion of the reaction.

The unreacted monomers and oligomers were removed from the obtained polymers by extracting with water. According to Reimschuessel,[14] the polymerized mixture of nylon 6 at an equilibrium consists of about 89 wt % polymer, 11 wt % unreacted CPL, and a small quantity of cyclic oligomers at 240°C. His result is in a good accordance with the yield of nylon 6 in Table II. As the POPD content increases, the polymerization yield becomes higher due to the reduction of the unreacted CPL.

Since the number of polymer molecules is half the sum of chain ends, the number-average molecular weights of block copolymers can be calculated from the concentrations of end groups. Table III shows the calculated molecular weights, which are in the range of 20,000–30,000 g/mol.

The solution viscosity is frequently used for estimating the molecular weights of polymers. In case of polyamides, the relative viscosity is usually adopted as a measure of molecular weight, and some relationships between the relative viscosity and molecular weight of polyamide have been reported in the literatures.[15,16] In Table III the relative viscosities of block copolyetheramides are significantly lower than that of the nylon 6 homopolymer, even though the number-average molecular weights of block copolymers are higher than that of nylon 6. Also as the soft segment content increases and the block length of soft segment becomes shorter, the relative viscosities become lower significantly. Lofquist et al.[17] reported the same phenomena for their nylon 6–polyoxyethylene block copolymers. As they pointed out, this is probably attributed to both the increased flexibility of the polymer chains afforded by the ether linkage in the soft segment and the changes in polymer–solvent interaction.

Figure 1 shows the IR spectra of CPL/D-4000 block copolymers. The incorporation of the POP unit to the nylon 6 backbone chain gives a strong IR absorption by the C — O — C stretching vibration at about 1100 cm^{-1}.[18] As the content of POPD in the feed increases, the absorption band at 1110 cm^{-1} becomes stronger.

The chemical structures of polymers can be specified more quantitatively by NMR analysis. Figure 2 shows typical NMR spectra of a nylon 6–POP block copolymer and nylon 6 homopolymer. The five methylene groups in the monomeric unit of nylon 6 have the respective different positions in NMR spectrum depending on degree of shielding of the proton attached to each methylene group. On the other hand, the NMR spectrum of the block copolymer displays three additional peaks at 1.2, 3.6, and

Table III Molecular Weights of Block Copolymers

| Sample	[COOH] mmol/kg	[NH₂]mmol/kg	M_n g/mol	η_{rel} (95% H_2SO_4)
N-6	49.5	55.3	19,000	2.43
D4-10	58.1	35.1	21,500	1.42
D4-20	55.0	32.1	22,900	1.27
D4-40	50.8	31.6	24,300	1.19
D4-60	66.1	22.9	22,500	1.16
D4-80	71.2	23.4	21,200	1.14
D20-10	64.6	48.9	17,600	1.75
D20-20	61.7	32.7	21,200	1.52
D20-40	52.0	22.5	26,800	1.35
D20-60	46.9	22.7	28,800	1.25
D20-80	50.9	14.4	30,600	1.21
D40-10	55.4	45.3	19,900	2.11
D40-20	46.8	35.4	24,300	1.65
D40-40	48.1	40.7	22,500	1.48
D40-60	40.7	20.5	32,700	1.32
D40-80	54.9	14.8	28,700	1.27

3.8 ppm as compared to that of nylon 6. These peaks become stronger as the POP content increases. In Figure 3 each NMR peak is assigned to the corresponding hydrogen in nylon 6–POP block copolymers. It is noteworthy that methylene peaks of the ADA unit are superposed on those of nylon 6 unit.
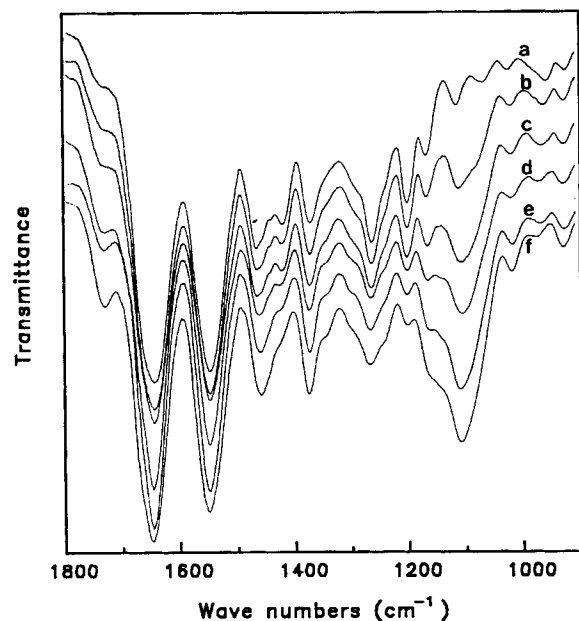
Figure 1 FT-IR spectra of CPL/POPD copolymers. (a) N-6, (b) D40-10, (c) D40-20, (d) D40-40, (e) D40-60, (f) D40-80.
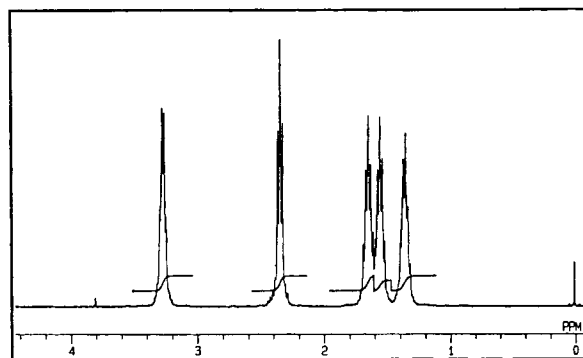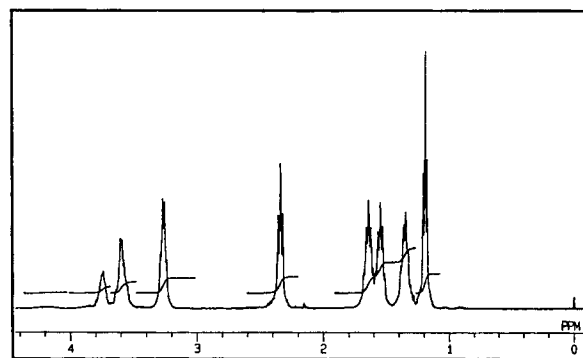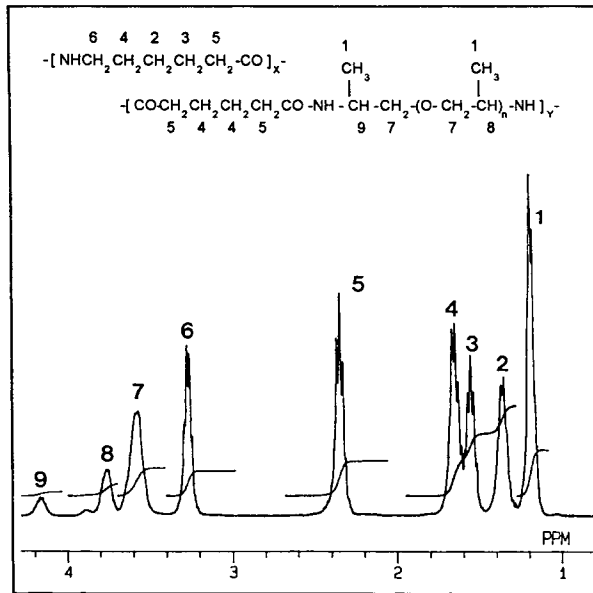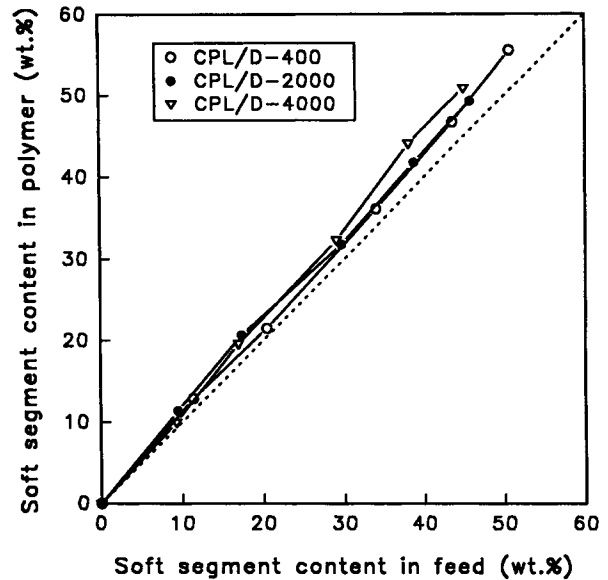

Figure 2 400 MHz ^{1}H-NMR spectra of (a) nylon 6 homopolymer and (b) nylon 6–POP copolymer in HCOOH/ $CDCl_3$ at room temperature.

6 4 2 3 5
-[NHCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$-CO]$_x$- $\overset{1}{CH_3}$ $\overset{1}{CH_3}$

-[COCH$_2$CH$_2$CH$_2$CH$_2$CO -NH - CH -CH$_2$-(O- CH$_2$-CH)$_n$-NH]$_y$-
  5   4   4   5   9   7   7   8

Figure 3 Typical ^{1}H-NMR spectrum of nylon 6–POP copolymer.

Figure 4 Feed composition vs. copolymer composition for the polymerization of CPL and POPD. The copolymer compositions were determined after the unreacted CPL and oligomer were extracted by water.

Since unreacted monomers and low-molecular-weight oligomers were removed by water extraction, the polymer composition might be different from the feed composition. Based on the NMR peak assignments as shown in Figure 3, the copolymer compositions were calculated from an integral of the areas under each of the resonance lines and are listed in Table IV. Explicitly there are some differences between feed and copolymer compositions. These differences are plotted in Figure 4. In all cases the POP content in copolymer is higher than that in the feed. Also as the block length and content of POP unit increase, the deviation between feed and polymer composition becomes larger. As mentioned previously, there exists unreacted CPL of about 11

Table IV Soft-Segment Content in Copolymer Determined by ^{1}H-NMR

Sample	Weight %		Mole %	
	Feed	Copolymer	Feed	Copolymer
D4-10	11.4	12.9	2.41	2.84
D4-20	20.5	21.5	4.68	5.11
D4-40	34.0	36.2	8.93	10.10
D4-60	43.6	46.7	12.90	14.70
D4-80	50.7	55.6	16.40	19.80
D20-10	9.5	11.4	0.54	0.65
D20-20	17.4	20.7	1.06	1.32
D20-40	19.7	31.9	2.11	2.34
D20-60	38.8	41.8	3.12	3.54
D20-80	45.8	19.3	4.12	4.73
D40-10	9.3	10.0	0.25	0.27
D40-20	17.0	19.6	0.50	0.59
D40-40	29.1	32.4	1.01	1.15
D40-60	38.1	44.1	1.50	1.88
D40-80	45.0	50.9	1.99	2.45

Table V Average Block Lengths of Soft and Hard Segments

Sample	Soft Segment		Hard Segment	
	No. of Unit	M_W of Segment	No. of Unit	M_W of Segment
D4-10	1.03	588	32.1	3,630
D4-20	1.05	602	18.1	2,040
D4-40	1.11	636	9.50	1,070
D4-60	1.17	670	6.57	743
D4-80	1.25	712	4.91	555
D20-10	1.01	2,230	87.6	9,900
D20-20	1.01	2,240	56.0	6,330
D20-40	1.02	2,260	35.0	3,960
D20-60	1.04	2,300	23.6	2,660
D20-80	1.05	2,320	21.3	2,400
D40-10	1.00	4,660	133.0	12,860
D40-20	1.01	4,680	90.5	10,230
D40-40	1.01	4,710	55.2	6,240
D40-60	1.02	4,740	52.6	5,950
D40-80	1.03	4,770	30.1	3,400

wt % within the polymer mixture after the completion of the reaction. Thus the extraction of the CPL would bring about the increase of POP content in the block copolymer. The composition of oligomer to be extracted may give rise to the changes of compositions. It is more probable that the soft segment with short-chain length such as D-400 could form readily oligomers by the reaction with CPL and thereby may be removed by water extraction. However, it seems that the soft segment with long-chain length such as D-4000 would not exist in the form of oligomers because it becomes high-molecular-weight polymers when reacted with a small amount of CPL. Therefore in case of CPL/D-4000 block copolymers the part removed by water extraction becomes smaller, resulting in higher soft-segment content in the polymer.

By using a statistical theory developed by Sorta and Melis,[19] the average block lengths of the hard and soft segments were determined. The copolymer compositions obtained from the NMR analysis and the molecular weights in Table III were used as a raw data in the calculation of the block lengths. The calculated values are listed in Table V. While the block lengths of soft segments correspond nearly to one POP unit, the block lengths of hard segments are varied with the content and chain length of the soft segment. As the soft-segment content decreases and the chain length of the soft segment increases, the hard block length becomes longer.

CONCLUSIONS

Nylon 6–POP block copolymers were synthesized by melt polymerization of CPL and POPD in the presence of water as a ring-opening catalyst. IR and NMR analyses indicate that the POP unit is incorporated into the nylon 6 backbone chain. The POP content in the copolymer composition is higher than that in the feed composition due to the removal of unreacted CPL by water extraction. The increase of the POP content in the copolymer enhances the polymerization yield and reduces the solution viscosity. The use of the POP unit with short-chain length facilitates the formation of low-molecular-weight oligomers, which could be removed by water extraction. The average hard block lengths in block copolymers are largely dependent on the size and content of POP units.

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