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Synthesis of Block Copolyamides by End-Reactive Oligomers

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ABSTRACT

Block copolyamides having poly(propylene oxide) units in main chains were prepared by interfacial polycondensation using hydroxyl-terminated poly(propylene oxide), acid chloride and diamine. Block copolyamides having poly(styrene) segments were also prepared by the same technique by using endcaped poly(styrene) with carboxyl or amine end groups. They were characterized by spectroscopic, thermal and X-ray analyses.

Platlet adhersion behaviors were evaluated on the surface of these block copolyamides and it was found that the platelet adhersion and aggregation were greatly influenced by the domain size as well as the distribution of the block units in the block polyamides. Biocompatibilities of these block polyamides were discussed in respect of microphase-separated domain structures.

INTRODUCTION

It has been known that synthetic polymers which have a microphase-separated structure similar to heterogenious endothelium surface[1], showed a good antithrombogenicity and various types of block copolymers including segmented poly(urethane)s[2] have been evaluated in terms of biomedical uses such as artificial organs. Blood coagulation is caused by the adhersion and aggregation of platelet on the surface of materials in contact with

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blood cells and a microphase-separated structure of block copolymers may have a great influence on the first step of the adhersion of blood platelet owing to some interactions with the surface of block copolymers.

This paper deals with the synthesis of block copolyamides having hydrophilic and hydrophobic segments such as poly(propylene oxide) and poly(styrene) as well as the characterization of these block copolyamides in respect of physical properties.

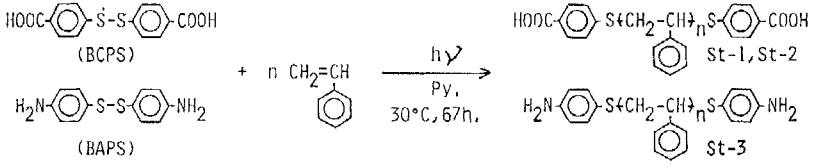
Adhersion behaviors of blood platelet were evaluated on the surface of these block copolyamides by a microshere column method, and the size and distribution of microphase-separated domains of block units were discussed in terms of antithrombogenetic effect on the surface structures.

MATERIALS

MONOMERS AND OLIGOMERS

Commercially available poly(propylene oxide) of molecular weight 3,000 which had hydroxyl groups on both ends was used as a hydrophilic segment of block copolyamides.

Endcaped poly(styrene)with carboxyl or amine end groups was synthesized by a radical polymerization in the presence of phenylene disulfides having carboxyl or amine groups as shown below:



Bis (4-carboxylphenyl or 4-aminophenyl) disulfides were dissolved with an excess amount of styrene in pyridine and the solution was irradiated with UV light from a high pressure mercury lamp at 30°C for 67 hr. After the irradiation the solution was evaporated in vacuum and residues were recrystalized from acetone and benzene.

TABLE 1

Synthesis of Telechlelic Poly(styrene)

Prepolymer	No.	Yield/%	Mw[a]	Functionality	$\eta_{sp/c}$[b]
$HOOC\text{-}St\text{-}_nCOOH$	St-1	10.2	7280	2.2	0.12
	St-2	29.4	9880	2.2	0.14
$NH_2\text{-}St\text{-}NH_2$	St-3	67.1	7650	1.9	0.09

a; Calculated from solution viscosity in benzene by $[\eta] = 3.64\times10^{-4} M^{0.64}$.
b; Measured in m-cresol at 30°C.

TABLE 2

Synthesis of Telechelic Polyamide

Prepolymer	No.	Yield/%	Mn[a]	Functionality	$\eta_{sp/c}$[b]
NH_2-Ny6-NH_2	Ny-1	60.8	4000	1.8	0.37
	Ny-2	68.2	6700	2.0	0.48

a; Determined by end-group titration.
b; Measured in m-cresol at 30°C.

Results of the synthesis of telechelic poly(styrene) are summarized in Table 1.

Telechelic polyamide with amine end groups was obtained by the ring-opening polymerization of ε-caprolactam in the presence of hexamethylenediamine as shown in Table 2.

$$NH_2(CH_2)_6NH_2 + \left[\begin{matrix}-NHCO-\\ (CH_2)_5\end{matrix}\right] \xrightarrow{260^\circ C,\ 5h}$$

$$NH_2(CH_2)_6\text{-}NHCO(CH_2)_5\text{-}_mNH_2$$

REAGENTS

All solvents were purified by conventional methods before use and dried.

Styrene and ε-caprolactam were purified by vacuum distillation. Sebacoyl chloride was synthesized from sebacic acid and thionyl chloride and was purified by vacuum distillation.

METHODS

POLYCONDENSATION

Block copolyamides having poly(propylene oxide) and poly(styrene) segments were prepared by interfacial polycondensation reaction. A typical procedure for the synthesis is as follows: 1.41g (0.47mmol) of poly(propylene oxide) of moleuclar weight of 3,000 was allowed to react with 5.42g (22.65mmol) of sebacoyl chloride at 80-90°C for 6 hr. Then, the reaction mixture was dissolved in 113 cm^3 of dry chloroform and the solution was rapidly poured with a vigorous stirring into an aqueous solution of 300 cm^3 containing 2.58g (22.18 mmol) of hexamethylenediamine and 1.77 g (44.25 mmol) of sodium hydroxide.

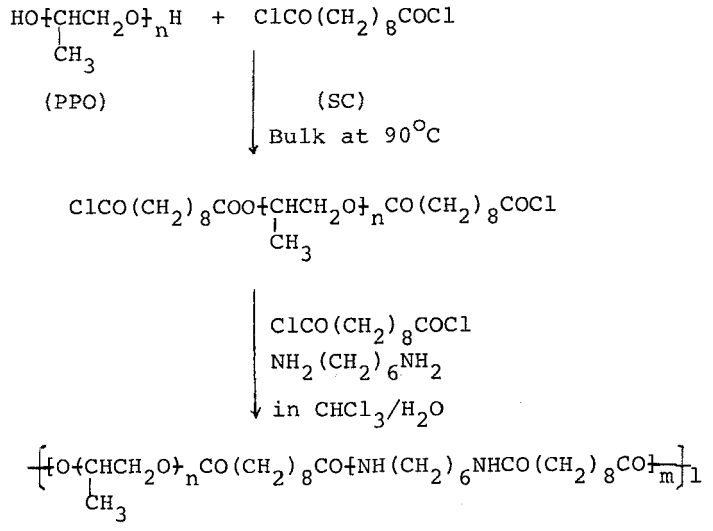
After the stirring for 5 min., the whole solution was poured into 800 cm^3 of methanol followed by keeping the solution for one day to remove unreacted PPO. Polymer was separated by filtration, followed by repeated washing with methanol and drying in vacuum.

Block copolyamides having poly(styrene) segments were prepared by reacting acid chloride-caped poly(styrene) which was obtained from acid-caped poly(styrene) with thionyl chloride, with oligo-nylon 6 having amino end groups at both ends. The polycondensation reaction was carried out in N-methyl pyrrolidone in the presence of triethylamine as an acid acceptor.

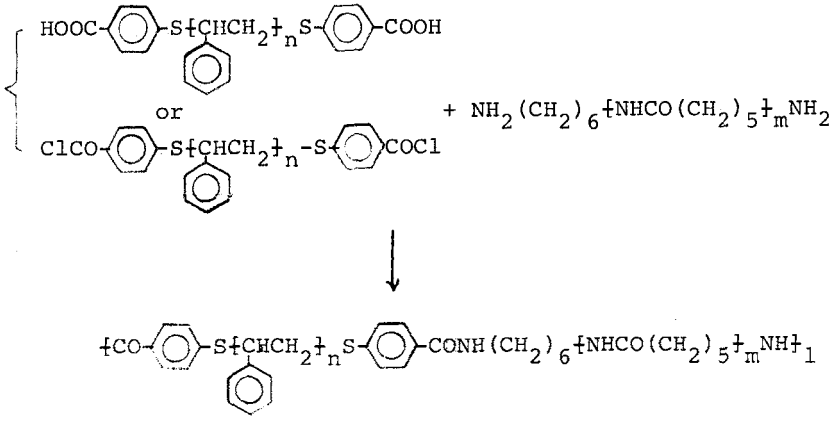
Direct polycondensation of two oligomers of acid-caped poly(styrene) and amine-ended nylon 6 was carried out in a solid phase at 160°C in vacuum. Melt polycondensation of these two oligomers was also tried at 247°C, which resulted in the formation of insoluble polymers owing to thermal decomposition.

The block copolyamides having poly(propylene oxide) and poly(styrene) segments were purified by repeated reprecipitation from N-methyl pyrrolidone and methanol, followed by drying in vacuum.

Synthetic routes are shown as follows:



Block copolyamides having poly(styrene) segments were synthesized by following different routes as follows:



1. Melt polycondensation
2. Solid phase polycondensation
3. High temperature solution polycondensation
4. Low temperature solution polycondensation in N-methyl pyrrolidone

CHARACTERIZATION

POLYMER STRUCTURE ANALYSES

Structures of the block copolyamides were identified by infrared and NMR spectra and by elemental analyses. Molecular weight distribution was measured by a gel permeation chromatogrphy (GPC), which was carried out by WATERS model 150ACC instrument by using columns of SHODEX AD-80M/S and AD-802/S. m-Cresol was used as a solvent for GPC with a column temperature of 100°C and a flow rate of 1.0 cm^3/min.

Thermal properties of the block copolyamides were measured by a differential scanning calorimetry (DSC) with RIGAKUDENKI model 8261DI and PTC-6D calorimeters at a heating rate of 20°C/min.

Both wide- and small angles X-ray diffractions were measured by RIGAKUDENKI model RU-200 X-ray analyser with a nickel-filtered Cu K_α radiation by runing at 50 kV and 200 mA.

Dynamic mechanical properties were measured by a Vibron Dynamic Viscoelastometer in temperature ranges between -100° and 200°C with a frequency of 11 Hz after films were obtained by casting m-cresol solutions of the block copolyamides.

Films of the block copolyamides were stained with Osminium tetraoxide and microstructures of film surfaces were observed by a scanning electron microscope (HITACHI HS-9) so as to determine micro-phase separated structures.

EVALUATION OF PLATELET ADHERSION

Fresh blood of 3 cm^3, which was collected from a jugular vein of a mongrel dog by a disposable syringe, was immediately passed through a column packed with glass beads which were coated with the block copolyamides films. The coating was carried out by soaking the glass beads in 0.1% polymer solution in m-cresol, followed by drying in vacuum. Flow rates were adjusted at 1.2 cm^3/min with a

Presidol model 5003 infusion pump. Eluded blood was collected in a sample bottle containing 0.1 cm^3 of sodium citrate as an anticoagulant. The column was washed with saline solution at a flow rate of 1.2 cm^3/min in a period of 120 sec. The glass beads were placed in saline solution containing 1.25wt% of glutaraldehyde in order to fix adhered platelets on the beads. The beads were freez-dried, followed by coating with gold and the surfaces were observed by a scanning elecrton microscope.

The number of platelets in the eluded blood from the column was counted according to the method of Brecher and Cronkite.[3]

RESULTS AND DISCUSSION

SYNTHESIS OF BLOCK COPOLYAMIDES HAVING PPO UNITS

Table 3 summarizes results of the synthesis of block copolyamides having poly(propylene oxide) segments with different molecular weights. Solution viscosities of resulting polymers were sufficiently high enough to obatin thin films by casting methods, as shown in Table 3.

Results of elemental analysis of the polymers were in close agreement with expected analytical values, as can be seen in Table 3.

Infrared spectrum of the polymers exhibited absorptions owing to amide and ester linkages at 1730, 1640, and 1540 cm^{-1}, respectively, as shown in Figure 1.

NMR spectrum also verified the existence of poly (propylene oxide) segments and amide linkages.

Therefore, it is presumed that the polymers consist of block copolyamides which are linked by amide and ester linkages, as was expected from the synthetic route. However, the contamination of oligo-nylon610 which was difficult to separate from the polymers might be possible and GPC analysis was carried out in order to check to possibility of the contamination.

Table 3 Syntheses of PPO-segmented Polyamides

Sample	Elemental analysis (wt%)				Weight fraction of PPO[1]	Molecular weight		$\eta_{sp/c}$[3]
		C	H	N		PPO	Polyamide[2]	
61P1-17	found	65.8	10.5	7.1	0.17	1170	5000	2.31
	calcd	67.0	10.5	8.0				
61P1-36	found	65.7	10.3	5.8	0.36	1170	1800	1.61
	calcd	66.0	10.4	6.5				
61P1-65	found	63.8	10.2	2.5	0.65	1170	500	2.14
	calcd	63.6	10.2	2.2				
61P2-11	found	66.7	10.7	8.7	0.11	2000	17000	1.01
	calcd	67.3	10.6	8.6				
61P2-31	found	65.5	10.5	6.5	0.31	2000	4400	1.52
	calcd	66.0	10.5	6.4				
61P2-78	found	62.7	10.3	1.5	0.78	2000	600	1.53
	calcd	62.9	10.2	1.1				
61P3-10	found	68.6	9.9	9.2	0.08	3000	33200	1.68
	calcd	68.8	8.9	9.1				
61P3-25	found	61.5	9.7	6.8	0.25	3000	9200	2.05
	calcd	68.0	9.1	8.0				
61P3-47	found	64.8	10.2	5.0	0.47	3000	3400	1.55
	calcd	65.2	9.7	4.2				

1) Weight fraction of PPO in copolymer was determined by elemental analysis.
2) Molecular weight of polyamide segment was determined by elemental analysis.
3) 0.1g/10cm^3 in m-cresol at 30°C.

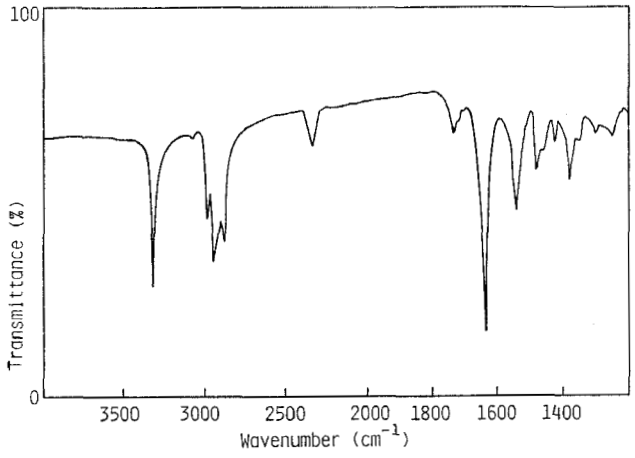


Figure 1 Infrared spectrum of the block copolyamide having PPO segments (P-25).

Figure 2 indicates GPC curves for PPO and the block copolyamide which contains 0.56 weight fraction of PPO segments. There is only one elution peak for the copolyamide, which is shifted toward higher molecular weight side in comparison with the peak for PPO, as seen in Figure 2. These results support the designed structure as the block copolyamide having PPO segments which are linked by ester linkages.

Thermal analyses of the block copolyamides showed two endotherm peaks at -60^{o} and at about 220^{o}C. The first peak corresponded with the glass transition temperature (T_g) of PPO segments and second one with the melting point (T_m) of nylon 610 segments, as shown in Table 4.

Table 4 indicates that T_g for the PPO segments and T_m for the polyamide segments do not change with increasing weight fraction of the PPO units in the copolymers, while the peak owing to T_g of the polyamide segments at 55.8^{o}C disappears in the copolymers. Perhaps, heat change at T_g of the polyamide segments might be absorbed by the PPO segments to bring a broad peak around T_g temperature areas.

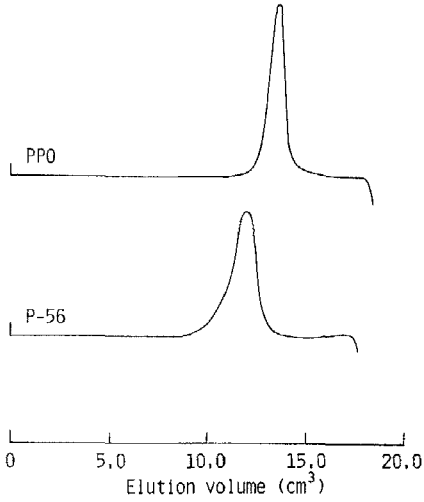


Figure 2 GPC analysis of PPO and the block copolyamide (P-56).

Table 4 Thermal Analyses of PPO-segmented Polyamides

Polymer	Tg for PPO (°C)	Tg for polyamide (°C)	Tm for polyamide (°C)
nylon610	-	55.8	219
P-10	-65.0	-	222
P-25	-52.0	-	223
P-47	-65.0	-	222
P-56	-62.0	-	218
PPO	-62.5	-	-

Behaviors of dynamic mechanical relaxation of the block copolyamides were observed by a Vibron viscoelastometer in the temperature ranges of -100 and 200°C and results are shown in Figure 3 , indicating as functions of storage mudulus (E') and loss modulus (E'') against temperatures. As can be seen in Figure 3, two peaks appear at around -60° and 40-60°C for temperature dependences of E' and E''. The first peak corresponds with T_g of the PPO segments and the second one with T_g of the polyamide segments. Figure 4 summarizes the dependence of T_g of these segments on the weight fraction of the PPO

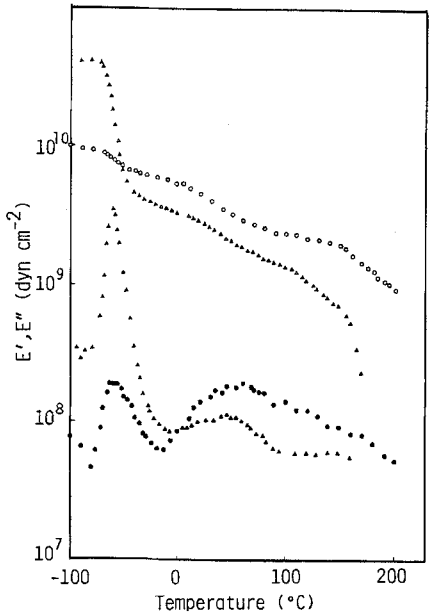
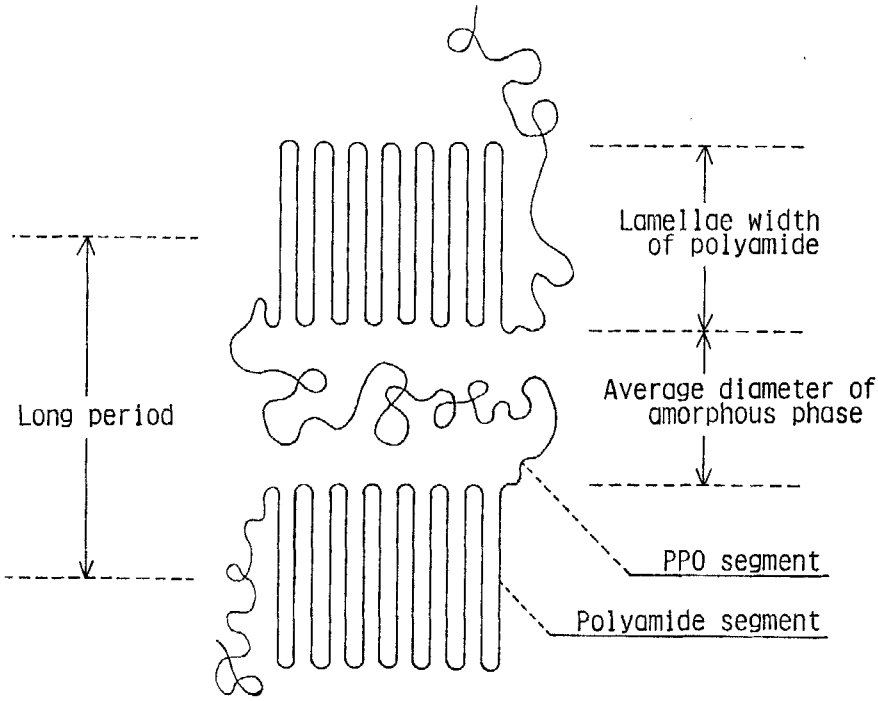


Figure 3 Temperature dependences of E' and E" of PPO-segmented polyamides.
Open plot, E'; closed plot, E"; (o), 61P3-10; (▲), 61P3-47.

units in the block copolyamides. Values of T_g for both PPO and polyamide segments do not significantly change up to the weight fraction of PPO of 0.5, while T_m and T_g of the polyamide segments drop above the weight fraction of 0.5.

These results strongly support that the obtained polymers consist of block units of PPO and polyamide segments in main chains, which form microphase-separated domains.

Wide- and small-angles X-ray scattering was carried out on these PPO segmented copolyamides and results are summarized in Table 5 where Bragg's spacings, long periods and Lamellae widths of crystalline parts of the polyamide segments, are shown as illustrated as follows:



X-Ray refraction patterns of the polyamide segments were basically the same as homopolyamide, nylon 610, and the space distances of the crystalline structures were almost the same as shown in Table 5. However, long period distances and Lamellae width tended to change with increasing content of the PPO segments. These results suggest that the distribution of amorphous and crystalline phases is influenced by the content of the PPO and polyamide segments, resulting in the formation of different microphase-separated structures.

SYNTHESIS OF BLOCK COPOLYAMIDES HAVING P-St UNITS

Table 6 summarizes results of the synthesis of block copolyamides having polyamide (nylon 6) and poly(styrene) segments, where polyamide having one terminal amino group reacted with telechelic poly(styrene) to form AB type block copolyamides. ABA type block copolyamides were

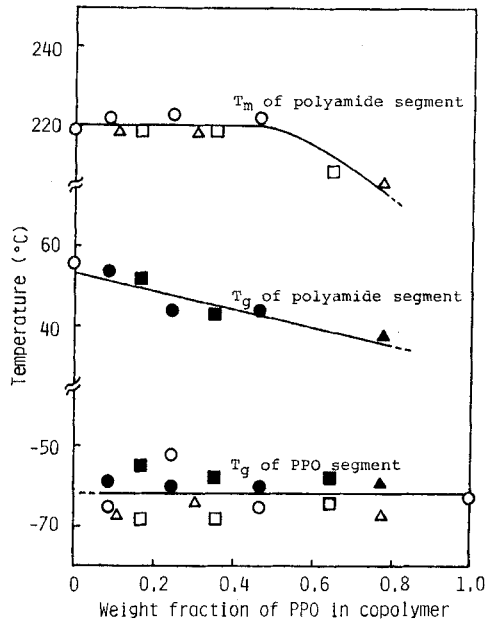


Figure 4 T_g and T_m of PPO segmented polyamides. open plot, measured by thermal analysis; closed plot, measured by dynamic mechanical properties; (□), 61P1 series; (△), 61P2 series; (○), 61P3 series.

Table 5 Microstructures of PPO-segmented Polyamides

Sample	Bragg's spacing (nm)[1]				Long period[2] (nm)	Lamellae width[3] of polyamide (nm)
	d	d'	d"	d"'		
nylon610	0.37	0.40	0.45	0.86	9.90	7.50
61P1-17	0.37	0.41	0.44	0.87	11.4	7.09
61P1-36	0.37	0.41	0.44	0.86	12.3	5.69
61P1-65	0.37	0.41	0.44	0.90	20.2	4.90
61P2-11	0.37	0.41	0.44	0.85	9.90	6.60
61P2-31	0.37	0.41	0.44	0.85	12.8	6.40
61P2-78	0.37	0.41	0.44	0.92	23.8	3.61
61P3-10	0.37	0.40	0.44	0.83	10.6	7.31
61P3-25	0.37	0.40	0.44	0.85	11.6	6.42
61P3-47	0.37	0.41	0.45	0.86	14.6	5.53

1) measured from wide-angle X-ray diffraction pattern.
2) measured from small-angle X-ray scattering pattern.
3) $=L \phi \chi_c$, where L is a long period, ϕ is a volume fraction of nylon 610, and χ_c is a degree of crystallinity of nylon 610 (=0.758)

Table 6 Syntheses of Nylon 6-Styrene $(AB)_n$ type block copolymers

Copolymer	prepolymer	Yield/%	Weight fraction of Nylon 6	Elemental analyses /% N	C	H	(Calcd.)	$\eta_{sp/c}$ a)
NS-21	St-2,Ny-1	68	0.21	3.0 (2.7)	79.3 (85.7)	7.6 (8.0)		0.20
NS-24	St-2,Ny-2	64	0.24	1.5 (3.0)	87.6 (84.9)	7.9 (8.1)		0.20
NS-28	St-2,Ny-3	86	0.28	4.1 (3.7)	81.8 (83.5)	8.3 (8.2)		0.41

a)0.1g/10cm^3 in m-cresol at 30°C.

also synthesized from nylon 6 having two end-amino groups and telechelic poly(styrene) and results are shown in Table 7.

All copolyamides were able to form thin film by casting though solution viscosities were in the range of 0.2 and 0.5. Elemental analyses of the copolyamides were in close agreement with expected values as shown in Tables 6 and 7. GPC analysis of the block copolyamides showed one sharp peak which shifted toward higher molecular weight region than that of starting oligomers of nylon 6 and poly(styrene). Therefore, the obtained polymers were not the blend of two oligomers, but the block copolyamide as expected from the reaction scheme. Figure 5 indicates a typical example of the GPC analysis.

PLATELET ADHERSION AND DEFORMATION

Behaviors of platelet adhersion and aggregation on the surface of the block copolyamides were investigated by using fresh blood of six dogs according to the column method and the total amount of adhered platelets was counted as shown in Table 8, which indicates that the amount of adhered platelets minimizes for the copolyamide containing 0.25 wt fraction of the PPO segments.

Shapes of the adhered platelete on the surface were observed by a scanning electron microscope as shown in Figure 6. It is seen in Figure 6 that the shape of the adhered platelet on the surface of nylon 610 deforms

Table 7 Syntheses of Nylon 6-Styrene ABA type block copolymers

Copolymer	Prepolymer	Yield/%	Weight fraction of Nylon 6	Elemental analyses /% N	C	H	(Calcd.)	$\eta_{sp/C}$[a]
NSN-1-46	St-1,Ny-5	81	0.46	5.9 (5.8)	76.8 (78.5)	8.5 (8.6)		0.21
NSN-1-55	St-1,Ny-6	84	0.55	7.1 (6.9)	73.3 (76.0)	8.9 (8.8)		0.37
NSN-1-64	St-1,Ny-7	83	0.64	7.9 (8.0)	72.0 (73.6)	8.9 (9.1)		0.40
NSN-1-71	St-1,Ny-8	94	0.71	9.0 (8.8)	68.1 (71.8)	9.0 (9.1)		——
NSN-2-39	St-2,Ny-5	72	0.39	5.1 (4.9)	78.6 (80.7)	8.5 (8.4)		0.22
NSN-2-48	St-2,Ny-6	81	0.48	6.2 (5.9)	74.8 (78.3)	8.5 (8.6)		0.38
NSN-2-64	St-2,Ny-8	85	0.64	8.1 (8.0)	70.9 (73.7)	8.9 (9.0)		0.42

a)0.1g/10cm^3 in m-cresol at 30°C.

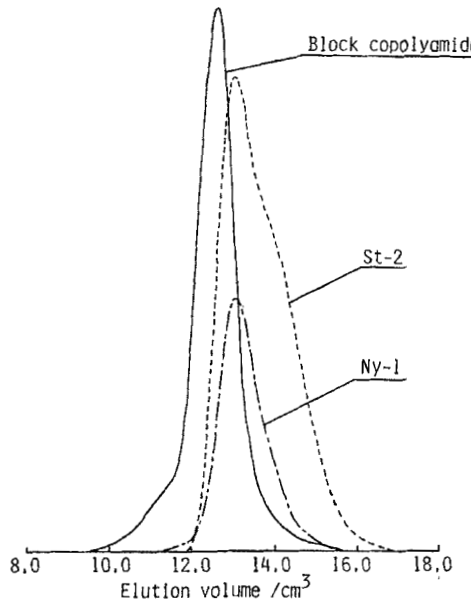
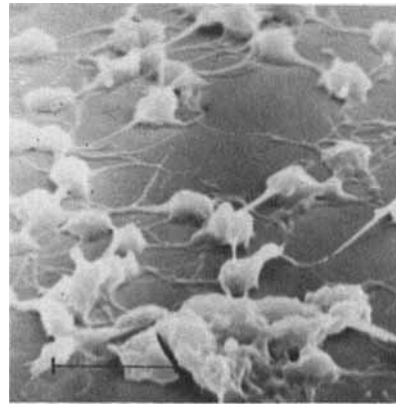


Figure 5 GPC elution pattern of block copolyamide by low temperature polycondensation. Solvent, m.-cresol; Temp., 100°C; column, Showdex AD-80M/S + AD-802/S.

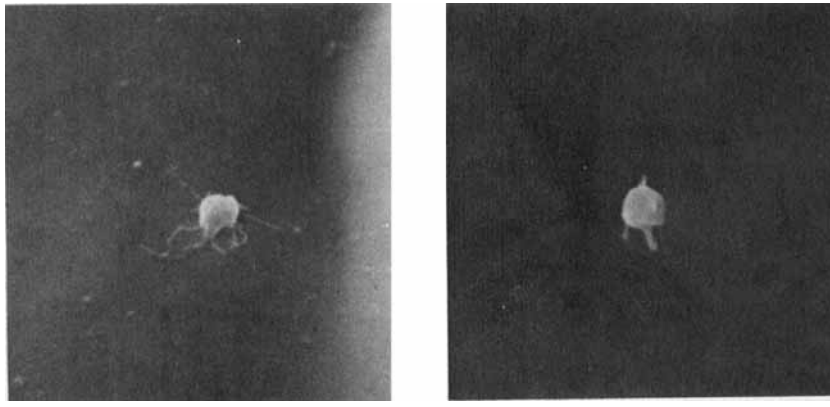
Table 8 Platelet Adhesion on the Surfaces of PPO-Segmented Polyamides

Polymer	Amount of adhered platelets (%) [a]
nylon610	27.2 ± 9.6
P-10	24.3 ± 7.8
P-25	14.1 ± 2.4
P-47	33.9 ± 11

a) The mean ± S.E.M. 100%=whole blood



Nylon 610



P-10 P-25 5μm

Figure 6 Scanning electron micrographs of the adhered platelet on the surface of nylon 610 and block copolyamides P-10 and P-25.

with the deployment of psudopods and each platelets aggragate to form a network structure. On the other hand, it was observed that a few number of platelets was adhered on the surface of the block copolyamides, especially on the surface of P-25 which contained 0.25 wt fraction of the PPO segments. The shape of the adhered platelets on the surface of P-25 was preserved, keeping a discoid shape as shown in Figure 6. The shape change of the adhered platelets was consistent with the results of the total amount of the adhered platelete which showed a minimum amount for P-25. Therefore, the surface structure of the block copolyamides plays an important role on the platelet adhersion behaviors.

The suppression of the adhersion of platelete on the surface of the block copolyamides might be ascribed to a microphase-separated structure which is composed of crystalline nylon 610 and amorphous PPO domains. It is expected that the size distribution of two domains may have a great influence on the adhersion behaviors of platelets at the initial stage of interaction with the surface. Therefore, long periods of the crystalline nylon segments were plotted against the amount of the adhered platalets as shown in Figure 7. It is seen in Figure 7 that the amount of the adhered platelets minimizes for the copolyamide with a long period of crystalline part at 11.6 nm, which is P-25. This period corresponds with average diameters of crystalline domains of 6.42 nm and amorphous domains of 5.18 nm, respectively.

Platelet adhersion on the surface of block copolyamides having poly(styrene) segments is shown in Figure 8 and the shape deformation of the adhered platelets was also observed by a scanning electron microscope as shown in Figure 9. A minimum of the amount of the adhered platelets was found for the block copolyamides having 0.5 wt fraction of poly(styrene) units and the deformation of the adhered platelets was suppressed for the same copolyamide as shown in Figure 9.

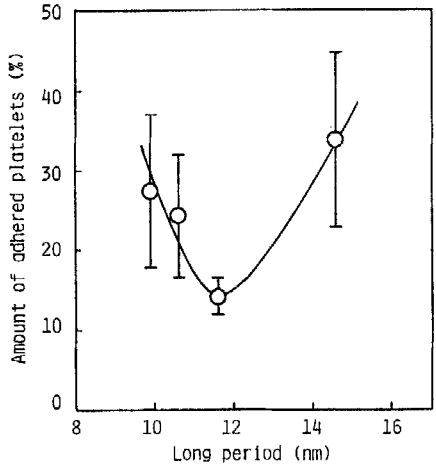


Figure 7 Relationship between the amount of adhered platelets and long period of crystalline region.

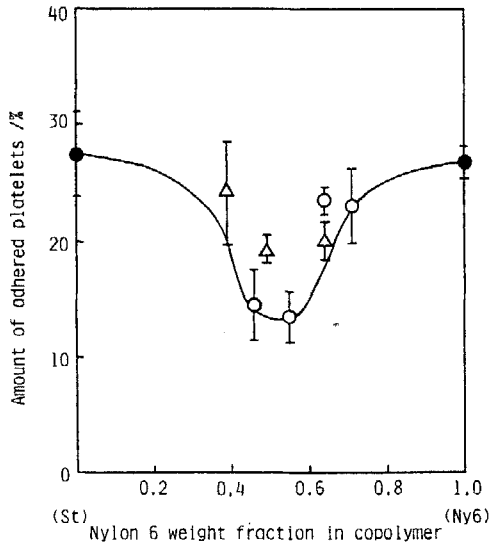


Figure 8 Amount of adhered platelets on the surface of Nylon 6-styrene ABA type block copolyamides. (o),Ny-St- 1-Ny; (Δ),Ny-St 2-Ny.

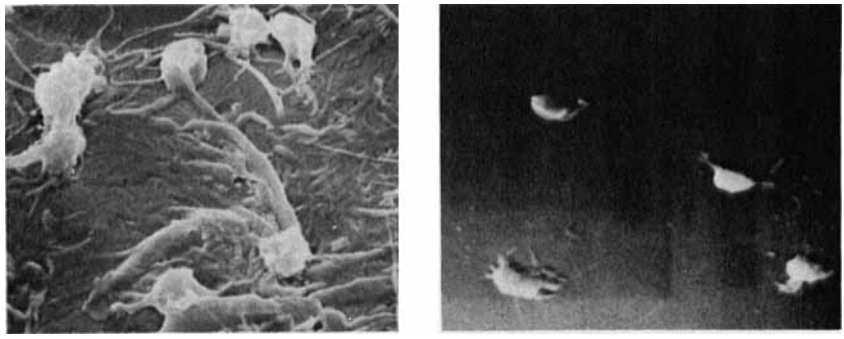


Figure 9 Scanning electron micrographs of adhered platelets on the surface of nylon 6 and NSN-1-64.

Minimum amount of the adhered platelets was found for the block copolyamides having PPO wt fraction of 0.25, while the block copolyamide having poly(sytrene) segments showed a minimum amount of adhered platelets at the wt fraction of 0.5 of poly(styrene) units. This reason may not only be ascribed to the size distribution of microphase-separated domains, but also to hydrophilic and hydrophobic characters of PPO and P-St domains.

Surface structure of the block copolyamide was observed by an electron microscope after the surface was stained with osminium tetraoxide and one of pictures is shown in Figure 10, which was taken for P-25. Block areas are composed of nylon 610 segments and white areas of PPO segments are formed as sea, indicating microphase-separated domain structures.

From these results the block copolyamides having PPO or P-St segments were found to form microphase-separated structures,and the size and the distribution of these domains greatly influenced on the platelet adhersion on

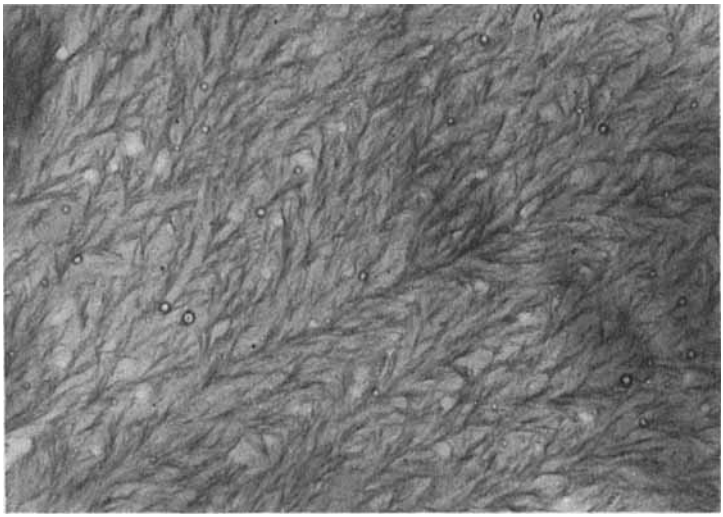


Figure 10 Electron micrograph of the surface of the block copolyamide P-25, stained with osminium tetraoxide.

the surface of these block copolyamides, as the case of block poly(urethane)[2] or block copolymers[4] from styrene and 2-hydroxyethyl methyl methacrylate.

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