Synthesis and Properties of Block Copolymers Based on Amine-Terminated Polydimethylsiloxane and Aromatic Polyamides

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ABSTRACT: Polysiloxane–aramid block copolymers were synthesized by a one-pot two-step method of direct polycondensation using triphenyl phosphite and pyridine as the condensing agent. Carboxyl-terminated aramid oligomers were prepared by the reaction of 3,4′-oxydianiline and isophthalic acid, and then condensed with bis(3-aminopropyl)polydimethylsiloxane giving the block copolymers with inherent viscosities of $0.21-0.41 \, dl \, g^{-1}$. They are soluble in amide-type solvents like N,N-dimethylacetamide and gave translucent and ductile films by casting from the solutions. These block copolymers start to decompose around 300°C.

KEY WORDS Polydimethylsiloxane–Aramid Block Copolymers / Direct Polycondensation / Solubility / Thermal Behavior / Tensile Properties /

We have studied the synthesis and properties of multiblock copolymers based on poly(oxyethylene)s[1] and polybutadiene[2] as the soft block, and aromatic polyamides (aramids) as the hard block. All these block copolymers have been conveniently obtained by the direct polycondensation of amine-terminated telechelic aramid oligomers (aramid diamines) with carboxyl-terminated telechelic soft block oligomers using triphenyl phosphite and pyridine as the condensing agents. Films of the block copolymers had transparent and ductile properties caused by pseudo-crosslinked structure between aramid blocks.

Polydimethylsiloxane is one of the promising oligomers for the preparation of block copolymers.[3] Although polysiloxane is well known as a high gas permeation material, it has low mechanical strength. We already reported that the rigid structure of the aramid blocks is apparently retained in the block copolymers to produce·a strong elastomeric pseudo-cross-linked material.[1,2] This technique should be applicable to the synthesis of polysiloxane–aramid block copolymers, whose mechanical properties should be greatly improved. Amine terminated telechelic polydimethylsiloxanes were commercially available and used in some block copolymers such as polysiloxane–polyurethane type.[4] In this article, we describe the synthesis of polysiloxane–aramid block copolymers from bis(3-aminopropyl)polydimethylsiloxane and carboxyl-terminated aramid oligomers.

EXPERIMENTAL

Materials

Bis(3-aminopropyl)polydimethylsiloxanes (PSX-diamines) **3** were supplied from Shin-etsu Chemical Co., Ltd., and Chisso Co., Ltd., whose number average molecular weight were 1720 and 5600, respectively. They were dried at 120°C for 1 h *in vacuo*. 3,4′-Oxydianiline
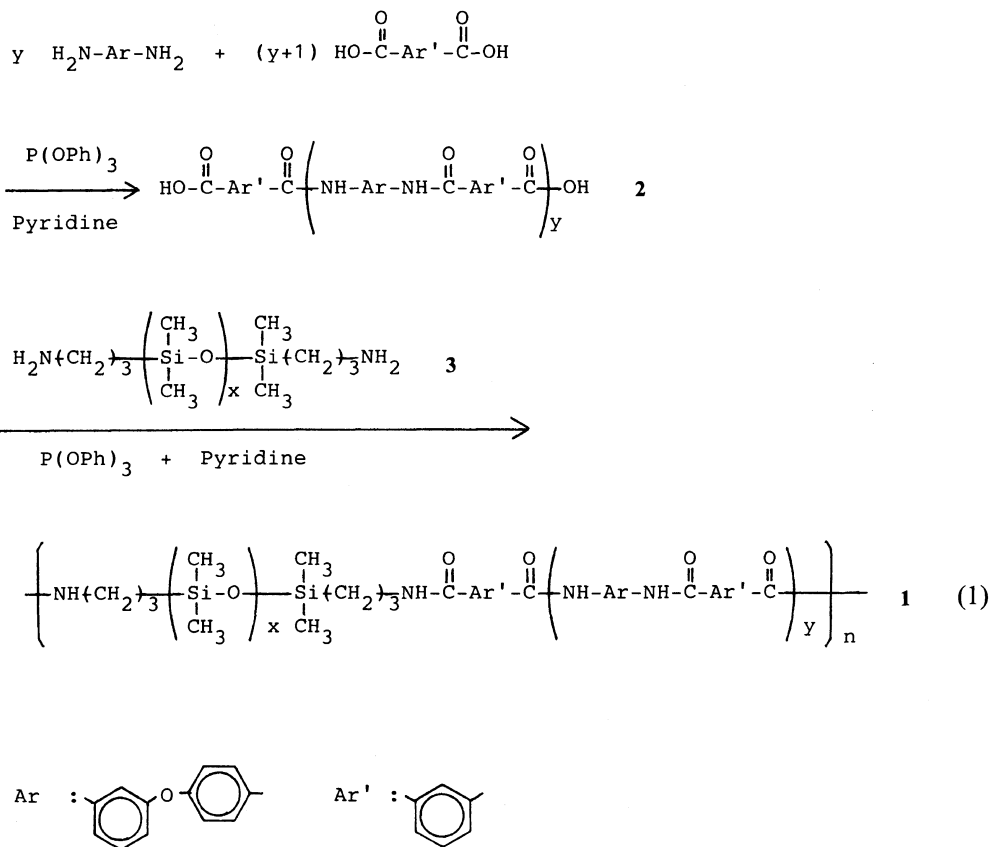
(3,4′-ODA) and isophthalic acid (IPA) were purified by recrystallization from chloroform–hexane and aqueous ethanol, respectively. Triphenyl phosphite, pyridine, N-methyl-2-pyrrolidone (NMP), and N,N-dimethylacet-amide (DMAc) were purified by distillation. Other organic and inorganic reagents were used as received.

Polymerization

Block Copolymer **1b**. A mixture of 3.00 g (15 mmol) of 3,4′-ODA, 2.66 g (16 mmol) of IPA, 9 ml of triphenyl phosphite, and 1.80 g of cetyltrimethylammonium chloride (CTMAC) in 36 ml of pyridine was heated with stirring at 100°C for 2 h under nitrogen. To this reaction solution, 1.72 g (1 mmol) of PSX-diamine ($\bar{M}_n = 1720$) and 9 ml of pyridine were added, and then the mixture was stirred for another

4 h at the same conditions. The resultant polymer was isolated by pouring the reaction mixture into 1 l of methanol. The product was purified by reprecipitation from DMAc-methanol, followed by successive washings with hot methanol and hot tetrachloro-methane and drying at room temperature *in vacuo*. The yield was 5.10 g (75%). The inherent viscosity of the polymer in DMAc was $0.33\,dl \cdot g^{-1}$, measured at a concentration of $0.5\,g \cdot dl^{-1}$ at 30°C. The infrared (IR) spectrum (KBr) exhibited absorptions at $3300\,cm^{-1}$ (N–H), $1650\,cm^{-1}$ (C=O), and 1100 ad $1020\,cm^{-1}$ (Si–O–Si). The ¹H-nuclear magnetic resonance (NMR) spectrum (D_2SO_4) showed peaks at 0 ppm (s, CH_3) and 6.6 —7.8 ppm (m, aromatic H).

Other block copolymers were prepared by similar procedures.

$$y \quad H_2N\text{-Ar-}NH_2 \quad + \quad (y+1) \quad HO\overset{O}{\underset{\|}{C}}\text{-Ar'-}\overset{O}{\underset{\|}{C}}\text{-OH}$$

$$\xrightarrow[\text{Pyridine}]{P(OPh)_3} \quad HO\overset{O}{\underset{\|}{C}}\text{-Ar'-}\overset{O}{\underset{\|}{C}}\left(\text{NH-Ar-NH-}\overset{O}{\underset{\|}{C}}\text{-Ar'-}\overset{O}{\underset{\|}{C}}\right)_y\text{OH} \quad \mathbf{2}$$

$$H_2N(CH_2)_3\left(\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-O}\right)_x\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}(CH_2)_3NH_2 \quad \mathbf{3}$$

$$\xrightarrow{\hspace{4cm}}$$
$$P(OPh)_3 \quad + \quad \text{Pyridine}$$

$$\left\{NH(CH_2)_3\left(\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-O}\right)_x\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}(CH_2)_3NH\overset{O}{\underset{\|}{C}}\text{-Ar'-}\overset{O}{\underset{\|}{C}}\left(NH\text{-Ar-}NH\overset{O}{\underset{\|}{C}}\text{-Ar'-}\overset{O}{\underset{\|}{C}}\right)_y\right\}_n \quad \mathbf{1} \quad (1)$$

Ar : [benzene ring]—O—[benzene ring]—   Ar' : [benzene ring]

Measurements

IR and ^{1}H NMR spectra were recorded on a Hitachi EP-G3 spectrophotometer and a JEOL Model FX-90Q Fourier transform spectrometer, respectively. Differential thermal analysis (DTA) and thermogravimetry (TG) were performed with Shimadzu thermal analyzers DTA-30M and TGA-30M, respectively. Differential scanning calorimetry (DSC) was performed with a Daini Seikosha SSC-560 differential scanning calorimeter. Tensile properties were determined from stress-strain curves obtained with a Toyo Baldwin Tensilon UTM-III at an elongation rate of 20% min^{-1}. Measurements were performed at room temperature on film specimens (5 mm wide, 35 mm long, and about 0.1 mm thick) and the average of at least five individual determinations was taken. Small-angle X-ray scattering were performed on a Rigakudenki RU-200 X-ray diffraction apparatus with nickel-filtered Cu-K_α radiation (50 kV, 200 mA).

RESULTS AND DISCUSSION

Synthesis of Block Copolymers

Polysiloxane-aramid block copolymers **1** were synthesized according to eq 1 by the one-pot two-step procedure reported previously.[1,2,5] PSX-diamines **3** used in this study had a number-average molecular weight ($\bar{M}_n$) of 1720 and 5600.

In the first step, the solutions of carboxyl-terminated aramid oligomers **2** with $\bar{M}_n$s from 1800 to 8000 were prepared by the reaction of a calculated excess of IPA with 3,4'-ODA in the presence of triphenyl phosphite and pyridine in NMP. PSX-Diamine **3** was then added to the just prepared polyamide solution, and polycondensation was continued to form polysiloxane-aramid block copolymers **1**.

Although direct polycondensation using triphosphite and pyridine in NMP proceeded in a homogenous solution in the synthesis of polyoxyethylene–aramid and polybutadiene–aramid multi-block copolymers, the prepration of polysiloxane–aramid block copolymers was unsuccessful under the same reaction conditions because of the insoluble nature of PSX-diamine **3** in the reaction medium. Some additives such as inorganic salts and ammonium salts were examined to improve the reaction system. For instance, lithium chloride, calcium chloride and triethyamine hydrochloride have been reported as effective additives to obtain polyoxyethylene–aramid and polybutadiene–aramid multiblock copolymers of higher molecular weight.[1,2,5] Table I shows the inherent viscosities of polysiloxane–aramid block copolymer **1b** when various reagnets were added to the reation medium, and it was found that cetyltrimethylammonium chloride (CTMAC)

Table I. Effects of additives on inherent viscosities

Additive	Yield	η_{inh}[a]
	%	dl g^{-1}
None	70	0.23
LiCl+CaCl$_2$	77	0.29
TEAHCl[b]	77	0.26
TEAC[c]	72	0.23
CTMAC[d]	76	0.32

[a] Measured at a concentration of 0.5 g dl^{-1} in DMAc at 30°C.
[b] Triethylamine hydrochloride.
[c] Tetraethylammonium chloride.
[d] Cetyltrimethylammonium chloride.

Table II. Effects of solvent composition on inherent viscosities

Solvent composition	Yield	η_{inh}[a]
NMP/Pyridine/Dioxane/Additive	%	dl g^{-1}
3/1/0/CTMAC[d]	76	0.32
0/1/0/TEAHCl[b]	77	0.30
0/1/0/CTMAC	75	0.33
3/1/1/CTMAC	76	0.27

[a–d] See footnote of Table I.

which should behave as a phase transfer catalyst was the most effective one, giving polysiloxane-aramid multi-block copolymers with an inherent viscosity of $0.32 \, dl \, g^{-1}$. Examination of the reaction media indicated that pyridine alone was a relatively good solvent as shown in Table II. Under these polymerization conditions, block copolymers **1** with inherent viscosities of 0.21—$0.41 \, dl \, g^{-1}$ were obtained (Table III). These values of inherent viscosities are not comparable to the molecular weights of the block copolymers, because DMAc, the solvent for viscosity measurement, is a good solvent for aramid and a poor solvent for polysiloxane. The observed viscosities should be somewhat lower in the block copolymers with high polysiloxane content compared with those of low polysiloxane content, if all block copolymers have nearly the same molecular weight.

The structure of the resultant block copolymers **1** was confirmed by means of IR and NMR spectroscopy, and elemental analysis. In the IR spectra, characteristic amide absorptions at $3300 \, cm^{-1}$ (N–H) and $1650 \, cm^{-1}$ (C=O), and two absorptions due to siloxane group at 1100 and $1020 \, cm^{-1}$ appeared. In the ^1H NMR spectra, two remarkable peaks at 0 ppm (Si–CH₃) and 7.2—7.7 ppm (aromatic H) were observed.

It was suggested from the results of NMR and elemental analysis (Table IV) that these block copolymers **1** were composed on the average of five units, *i.e.*, an aramid–PSX–aramid–PSX–aramid structure. The limitation of molecular weight of the present block copolymer is probably explained by the low solubility of polysiloxane oligomers in the reaction system and the low reactivity of aliphatic amine in direct polycondensation using triphenylphsphite and pyridine.[6]

Table III. Synthesis of polysiloxane–aramid block copolymers

Code	$\bar{M}_n$ of siloxane segment	$\bar{M}_n$ of aramid segment[a]	Siloxane content[a] %	η_{inh}[b] $dl \, g^{-1}$
1a	1720	7000	19	0.41
1b	1720	5000	25	0.33
1c	1720	3500	33	0.33
1d	1720	2500	41	0.29
1e	1720	1800	49	0.25
1f	5600	8000	41	0.30
1g	5600	5700	49	0.37
1h	5600	3800	60	0.37
1i	5600	2800	67	0.21
1j	5600	1800	76	0.21

[a] Calculated from feed ratio.
[b] Measured at a concentration of $0.5 \, g \, dl^{-1}$ in DMAc at 30°C.

Table IV. Elemental analysis and intensity of ^1H-NMR peaks of polysiloxane–aramid block copolymers

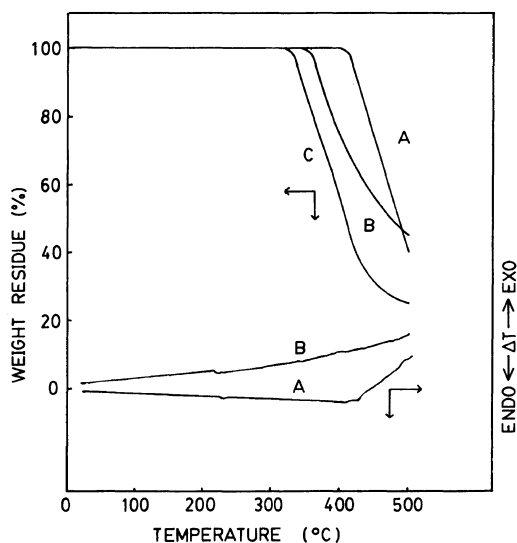| Block copolymer		Elemental analysis			Si–CH₃/Aromatics ratio
		C/%	H/%	N/%	
1b	Calcd. for $n = \infty$	63.10	5.29	6.58	0.71
	Calcd. for A[a]	65.60	5.00	7.03	0.48
	Calcd. for B[b]	67.00	4.83	7.28	0.35
	Found	64.29	4.67	6.90	0.47
1g	Calcd. for $n = \infty$	53.23	6.19	4.45	2.18
	Calcd. for A	57.18	5.79	5.23	1.45
	Calcd. for B	59.80	5.52	5.75	1.09
	Found	58.64	5.54	5.60	1.50

[a] Structure A: aramid–PSX–aramid–PSX–aramid.
[b] Structure B: aramid–PSX–aramid.

Properties of Block Copolymers

Polysiloxane-aramid block copolymers **1** were readily soluble in amide-type solvents such as DMAc and NMP, dimethyl sulfoxide, and pyridine. They were insoluble in other organic solvents including tetrahydrofuran, dioxane, chloroform, and benzene, which were good solvents for PSX-diamine. This solubility behavior was fairly comparable to that of the aramid homopolymer prepared by the reaction of equimolar amount of 3,4'-ODA and IPA in the presence of triphenyl phosphite and pyridine, whose inherent viscosity was 0.54 in DMAc. The translucent and flexible films of **1** could be cast from the DMAc solutions on Teflon sheet, while the cast film on a glass plate adhered strongly to the glass surface and was difficult to tear off.

Thermal behavior of the block copolymers **1** was evaluated by means of DTA, TG, and DSC. Figure 1 shows typical DTA and TG

Figure 1. DTA and TG curves in air for (A) aramid homopolymer, (B) block copolymer **1b**, and (C) PSX-diamine.

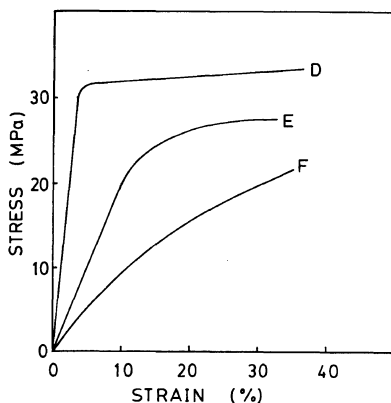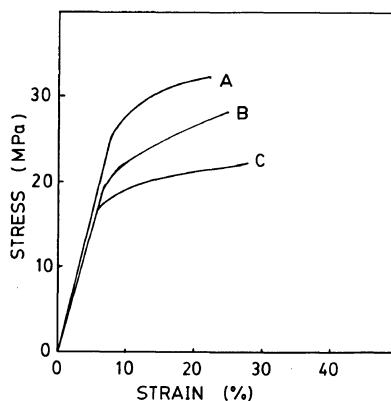**Table V.** Glass transition temperatures (T_g) of polysiloxane–aramid block copolymers

Polymer	T_g of poly-siloxane segment	T_g of aramid segment
	°C	°C
Aramid[a]	—	240
1a	−114	220
1b	−119	230
1c	−121	235
1d	−124	233
1e	−126	227
1f	−113	200
1g	−117	220
1h	−119	223
1i	−117	219
1j	−123	215
PSX-diamine[b]	−126	—

[a] The aramid homopolymer was prepared by polycondensation of 3,4'-ODA and IPA. The inherent viscosity was $0.54 \, dl \, g^{-1}$ measured at a concentration of $0.5 \, g \, dl^{-1}$ in DMAc at 30°C.

[b] Supplied from Chisso Co., Ltd. ($\bar{M}_n = 5600$).

Figure 2. Stress-strain curves for polysiloxane–aramid block copolymers **1a** (A), **1b** (B), **1d** (C), **1g** (D), **1i** (E), and **1j** (F).

Table VI. Tensile properties of polysiloxane-
aramid block copolymers

Polymer	Tensile strength	Elongation at break	Tensile modulus
	MPa	%	MPa
Aramid[a]	62	4.6	1400
1a	30	23	320
1b	28	25	300
1c	23	26	300
1d	22	27	280
1e	19	17	400
1f	24	30	750
1g	33	36	800
1h	22	34	500
1i	27	32	200
1j	21	35	100

[a] See footnote of Table V.

curves for the representative block copolymer, **1b**, as well as for the parent PSX-diamine **3** ($\bar{M}_n = 5600$) and aramid homopolymer. On the DTA curves in air, the onset of exothermic reaction was observed for all copolymers **1** around 300°C. The exothermic reaction was apparently due to the decomposition of polysiloxane units. This was supported from the TG curves, which revealed that the block copolymers **1** began to lose weight above 300°C in air.

In additon, a small endothermic peak, probably due to the glass transition of aramid segment, was observed on the DTA curves in the range of 200—235°C. These glass transition temperatures (T_g) were in good agreement with that of the aramid homopolymer (240°C).[7] The T_gs of the polysiloxane segment, evaluated by DSC, were in the range of $-121 \sim -124$°C, which agree well with that of polydimethylsiloxane homopolymer (-126°C). All thermal results are summarized in Table V. It was obvious that the T_gs of the polysiloxane phase increased with decreasing

polysiloxane content and those of the aramid phase decreased with decreasing aramid content in the block copolymers **1**. The fact, that two T_gs are in good agreement with those of the homopolymers, supports the phase separated structure of polysiloxane and aramid blocks.

Stress-strain curves of the polysiloxane-aramid block copolymer films are shown in Figure 2 and the tensile properties are summarized in Table VI. The films of block copolymers **1** had flexible and ductile characteristics only slightly dependent on the content of the aramid segment, while the tensile properties of films of the polyoxyethylene–aramid and polybutadiene–aramid multi-block copolymers were highly dependent on aramid content.[1,2,5] Low elongation at the break of these films was probably due to the rather low molecular weight of block copolymers **1** and inadequacy of the cast solvent (DMAc) for **1**.

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