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Copolymerization of aromatic polyamide macromonomers with methyl methacrylate

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Summary

Graft copolymers of end methacrylate-functionalized[MacroAM] or styrene-functionalized[MacroAS] polyamide macromonomers with methyl methacrylate(MMA) were prepared by radical copolymerization, and their thermal, dynamic properties, and miscibility with matrix PMMA have been investigated. The glass transition temperature(*Tg*)s of the copolymers were significantly elevated with the increase of the macromonomer content in the copolymer. Storage modulus *E*' of the graft copolymers began to decrease at around 85°C, which is close to *Tg* of PMMA, irrespective of the macromonomer content in the copolymers. As the macromonomer content and its degree of polymerization became higher, the drop in *E*' became significant.

Introduction

An effective improvement of surface properties of a polymer can be expected by blending a small amounts of surface active graft copolymer whose main chain or branch is miscible with the matrix polymers(1-2). The imcompatibility of the graft copolymer as a whole with the matrix polymer is important in surface modification.

While in order to improve the thermal and mechanical properties of a polymer, miscibility of the blending polymer with the matrix polymer is very important. Polyamide macromonomers derived from *p*- and *m*-aminobenzoic acids are considered rigid such branch components of a graft copolymer miscible with many base polymers obtained from conventional monomers. The authors reported the polymerizability of MacroAM and MacroAS synthesized by polycondensation of *p*- and *m*-aminobenzoic acids(7:3) in the presence of methacrylic acid or *p*-carboxystyrene using triphenylphospine-hexachloroethane as the condensation agent in pyridine(3-5). The *Tg* of the graft copolymer of the polyamide macromonomer with MMA was considerably improved by the presence of polyamide branches (6). However, there were problems about the low solubility and reactivity, specially with styrene, of the macromonomer in the copolymerization.

In this paper, detailed studies on the syntheses of more soluble aromatic polyamide macromonomers (*p*- : *m*-aminobenzoic acid=1 : 1 in molar ratio) of controlled degree of polymerization and copolymerization with MMA are reported, and the effects of the content and degree of the polymerization of macromonomers on the thermal and dynamic properties of the graft copolymer are examined.

Experimental

General

Proton NMR spectra were btained o a JEOL ^{1}NMR spectrometer model JNM-FX90A. The molecular weights and their distributions of the macromonomers and graft copolymers were estimated on a Nihon Bunko(JASCO) GPC model 805-GI with Shodex Asahipak column GF-7MHQ(exclusion molecular weight: pullulan 10,000,000) using poly(ethylene glycol)(*Mn*:150, 200, 580, 2,450, 18,000, 63,000, 66,000, 570,000 and 2,950,000) as the

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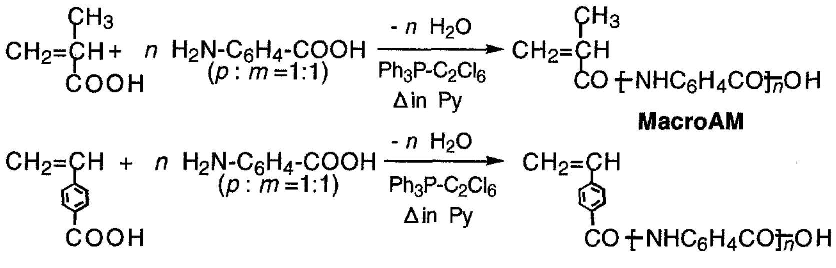
standard in dimethylformamide(DMF) containing 0.05 wt % lithium chloride and phosphoric acid(flow rate=0.5 ml/min) at 30°C. The number average degree of polymerization of the macromonomers was also estimated by ^{1}H NMR spectroscopy using the spectral area ratio of CH_3 or CH_2=CH- to -C_6H_4- for MacroAM and MacroAS, respectively. The composition of the copolymers was analyzed by ^{1}H-NMR spectroscopy. The DSC analysis of copolymers were carried out on a Rigaku Denki model DSC 8240 with the heating rate of 3°C /min.

Synthesis of aromatic polyamide macromonomers



MacroAM

MacroAS

Scheme 1. Synthesis of macromonomers.

Table 1. Synthesis of aromatic polyamide macromonomers[a)]

Macromonomer	Yield[c)] (%)	Solubility[d)] Soluble	Solubility[d)] Insoluble	*DP*, *n*[e)]	*Mw*[f)] /10²	*Mn*[f)] /10²	*Mw*/*Mn*
macroAM - 20[b)]	72	99	1	12	38	28	1.4
macroAM - 40	48	99	1	7	25	20	1.2
macroAS - 5	100	98	2	30	68	52	1.3
macroAS - 10	91	99	1	15	51	37	1.4
macroAS - 20	81	99	1	9	34	26	1.3
macroAS - 40	59	99	1	6	21	18	1.2

a) Aminobenzoic acid(0.1 mol; *p*- : *m*- = 1 : 1) was condensed in the presence of Ph_3P-C_2Cl_6 (0.1 mol) in pyridine (180 ml) for 4 h at 60°C.

b) The number indicates the mol % of the MA or PCS as a terminator to aminobenzoic acid.

c) Methanol insoluble fraction based on the starting materials.

d) One gram of macromonomer was dissolved in DMF(20 ml), and the insoluble fraction was separated by centrifugation. (12,000 rpm).

e) Degree of polymerization by ^{1}H NMR.

f) Molecular weights of DMF soluble fraction of polyamide macromonomer determined by GPC.

Macromonomers MacroAM and MacroAS were synthesized by polycondensation of a mixture of aminobenzoic acids (*p*- : *m*-=1 : 1) using a condensation agent of Ph_3P-C_2Cl_6-Py in the presence of methacrylic acid(MA) or *p*-carboxystyrene(PCS) according to the method previously reported(6).

Copolymerization of a macromonomer with MMA

Typical procedure is given. A macromonomer MacroAM-20(0.22 to 0.86 g (1.0x10^{-4} to 5.7x10^{-4} mol: 20 mol% of the macromonomer in the feed) and DMF(5 ml) were charged in a polymerization tube under nitrogen, and the content was agitated sufficiently until the macromonomer was dissolved completely. MMA(2.00 g, 0.02 mol) and AIBN(1.65x10^{-1}~1.69x10^{-2} g, 0.50 mol% to the feed monomers) were added therein. After enough agitation, the content was heated at 60°C for 24 h. The polymerization was stopped by pouring the content into methanol(100 ml). The formed polymer was subjected to centrifugal separation, dried under vacuum, and purified by reprecipitation(DMF-CH_3OH) for three times.

Results and Discussion

The results of the synthesis of macromonomers are shown in Table 1. DMF soluble macromonomers with narrow molecular weight distribution were obtained in good to reasonable yield. The degree of polymerization(*n*) of the macromonomers were in a range from 5 to 30. The results of graft copolymer synthesis are shown in Table 2. High yield was obtained in the copolymerization of MMA with MacroAM-20(n=12) when the latter was charged at a concentration of 0.4 mol % (No. 2) or 0.7 mol %(No.2 and 3). Both copolymers were soluble in DMF. The number average molecular weight was 60,000 for No.2 and 85,000 for No.3 with the distribution (*M*w/*M*n) of 1.3 and 1.5. The results of copolymerization of MacroAS with MMA were similar to the case of MacroAM with MMA. The GPC analysis of the copolymers proved that the macromonomer had quantitatively reacted and was incorporated in the copolymer.

The absolute values of *Tg* of the graft copolymers of MacroAM were significantly elevated compared with that of PMMA. This elevation in *Tg* of the copolymers is understood as a result of the interaction between the polyamide branches and the carbonyl groups in the PMMA main chain. The *Tg* of the copolymer 2 and 3 were 125°C and 127°C, respectively. *Tg* seemed to be raised somewhat with the increase in macromonomer content in the copolymer. When macromonomers of different degree of polymerization were used at the same concentration, the difference in *Tg* of the product polymer was not so large(132°C(No. 1) and 133°C(No. 4). The difference of degree of polymerization of the macromonomers is not large enough to differenciate the glass transition temperature.

The *Tg* of the copolymers of MacroAS with MMA was also significantly elevated. The difference in *Tg* did not change so much with the increase in macromonomer content[125 and 127°C, respectively with the concentrations of 0.4 mol% (No. 6) and 1 mol% (No. 7)] . The *Tg* of the copolymer from MacroAS-40 (n=6)(No. 5) was 128°C, and similar to that of the copolymer from MacroAS-10(n=15)(No. 9)(129°C), both are produced by 1 mol% charge. The difference of degree of polymerization of the macromonomers is not large enough to differenciate the glass transition temperature even in this case.

Films of the copolymers were prepared by solution casting to study the transparency and self-standing property. In the case of MacroAM-MMA copolymers, a transparent and self-standing film could be prepared when the macromonomer content was low (No. 2). However, with the increase in macromonomer content, the transparency of the film tended to be deteriorated, and became turbid and brittle in spite of high enough molecular weight (No. 3 and 4). On the other hand, in the case of MacroAS-MMA copolymers, excellently self-standing and transparent films were obtained (Nos. 5-7) except for the case of 3 mol% macromonomer content (No. 8). The transparency of the films tended to deteriorate as the macromonomer content was further increased. There seems to be a certain limit of the concentration of the macromonomer component to obtain transparent materials.

Temperature dependence of storage modulus *E*' was examined for MacroAS-MMA copolymers(Fig. 1) . *E*' began to decrease at a temperature near 85°C, which reflected the *Tg* of matrix PMMA, regardless of the macromonomer content in the copolymers. The decrease was moderate with lower concentration and molecular weight of the macromonomer, which suggests that the amide segments in the side chains are partially compatible with main chain PMMA.

Table 2. Copolymerization of macromonomers with MMA[a] and the properties of the formed graft copolymers

No	Macromonomer mol%(wt%)	n[b]	Yield[c] (%)	Composition[d]	Mw[e] x10^{-5}	Mw/Mn	Tg (°C)	Turbidity[f]	Film[g] Transparency	Film[g] Self-supporting property
1	MacroAM - 40 3 (20)	7	93	2	1.7	1.6	132	-	-	-
2	MacroAM - 20 0.4(5)	12	89	-	0.79	1.3	125	None	○	○
3	MacroAM - 20 0.7(10)	12	91	1	1.3	1.5	127	None	Turbid	×
4	MacroAM - 20 3 (30)	12	93	3	2.5	1.8	133	Turbid	Turbid	×
5	MacroAS - 40 1 (10)	6	91	1	0.56	1.3	128	None	○	○
6	MacroAS - 20 0.4 (5)	9	87	-	0.95	1.4	125	None	○	○
7	MacroAS - 20 1 (10)	9	86	1	1.7	1.9	127	None	○	○
8	MacroAS - 20 3 (30)	9	94	3	1.6	2.9	131	Turbid	Turbid	×
9	MacroAS - 10 1 (20)	15	90	1	1.7	2.3	129	-	-	-
10	MacroAS - 5 0.7 (20)	30	90	-	2.8	1.6	128	-	-	-

a) Macromonomer(0.22 ~0.86g, 0.134~0.116 mmol) and comonomer(2.0g, 0.02mol) were reacted in DMF(5 ml) at 60°C for 20h.

b) See Table 1.

c) Methanol insoluble part.

d) Mol % of macromonomer by ^{1}H NMR.

e) Determined by GPC for DMF soluble fraction using PSt standard.

f) As 20% DMF solution.

g) Cast film from 20% DMF solution.

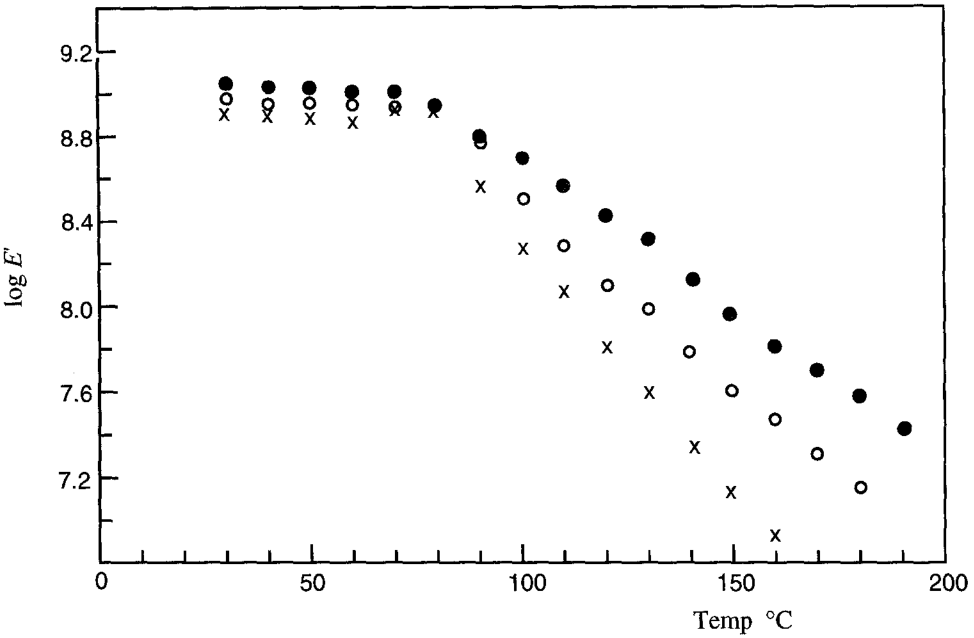


Figure 1. Temperature dependence of storage modulus E' of graft copolymers of Macromonomer with MMA

● MacroAS-40(No 5 in Table 2) ○ MacroAS-20(No 6) x MacroAS-20(No 7)

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Reference

1. Kawakami Y, Murthy R A N, Yamashita Y(1984) Makromol Chem **185**:9
2. Kawakami Y, Aoki T, Yamashita Y(1985) Macromolecules **18**:580
3. Yamazaki N, Higashi F, Kawabata J (1974) J Polym Sci-Polym Chem Ed **12**:2149
4. Yamazaki N, Niwano M, Kawabata J, Higashi F (1975) Tetrahedron **31**:665
5. Wu G C, Tanaka H, Sanui K, Ogata N(1982) Polym J **14**:571
6. Izawa M, Nunomoto S, Kawakami Y(1993) Polym J **25**:873