Synthesis and polymerization of isopropenyltriazines containing two alkyl groups and side-chain crystallization of the resulting polymers

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2,4-Bis(*N*-ethylanilino)-6-isopropenyl-1,3,5-triazine (BEIT) and 2,4-bis(*N*-octadecylanilino)-6-isopropenyl-1,3,5-triazine (BOIT) were prepared by the alkylation reaction of 2,4-dianilino-6-isopropenyl-1,3,5-triazine with the corresponding alkyl halides in the presence of sodium hydride in dimethylsulphoxide. The homopolymerization of these monomers and their copolymerization with styrene or methyl methacrylate were carried out using azobisisobutyronitrile as the initiator in benzene. The monomer reactivity ratios (r_1 and r_2) were determined for these monomers. The homopolymerization rate and the monomer reactivity in the copolymerization for BOIT were lower than those for BEIT. For the polymers from BOIT, exothermic crystallization peaks and endothermic melting peaks based on the side chains of the comb-like polymers were observed in differential scanning calorimetry thermograms. The crystallinity of the side chains decreased with increasing content of styrene or methyl methacrylate in the copolymers.

(Keywords: isopropenyltriazines; long alkyl group; monomer reactivity ratio; comb-like polymer; side-chain crystallization)

INTRODUCTION

Because the introduction of a long alkyl group as the side chain in polymers results in remarkable changes of thermal, mechanical and solution properties, comb-like polymers have been extensively studied[1-15]. In particular, the ability of side-chain crystallization has been actively investigated.

In our previous papers[16,17], we reported the synthesis and polymerization of 2-amino-4-(*N*-alkylanilino)-6-isopropenyl-1,3,5-triazines containing a long alkyl group, and found that the long alkyl side chains in the resulting comb-like polymers could be crystallized in a similar manner as conventional comb-like polymers in spite of the high glass transition temperature (T_g) of the main chain. We also showed that the homopolymerization rate and the monomer reactivity in copolymerization were independent of the alkyl chain length.

In order to explore the effects of two long alkyl groups on the polymerization behaviour and the properties of the polymer, this paper deals with the synthesis, homopolymerization, copolymerization and side-chain crystallization of the resulting comb-like polymers for 2,4-bis(*N*-octadecylanilino)-6-isopropenyl-1,3,5-triazine.

EXPERIMENTAL

Materials

2,4-Dianilino-6-isopropenyl-1,3,5-triazine (DAIT) was prepared from 1,5-diphenylbiguanide with methacryloyl chloride as described in the previous paper[18]. Dimethylsulphoxide (DMSO), tetrahydrofuran (THF) and benzene were purified by the usual methods and distilled over calcium hydride under nitrogen. Sodium hydride as a suspension in paraffin and alkyl halides were commercially available and used without further purification. Styrene (St) and methyl methacrylate (MMA) were commercially available and purified by the usual procedures.

Measurements

^{1}H n.m.r. spectra were recorded on a Hitachi R-600 spectrometer operated at 60 MHz in $CDCl_3$, and the chemical shifts are given as δ values in ppm from tetramethylsilane (TMS) as an internal standard. Melting points (m.p.) of monomers and T_g of polymers were determined by differential scanning calorimetry (d.s.c.) on a Rigaku-Denki DSC-8230 at a heating rate of 20°C min^{-1}. D.s.c. in the low-temperature region was measured from -120 to 100°C on a Rigaku-Denki Thermoflex with a low-temperature unit at heating and cooling rates of 10°C min^{-1}. Molecular weights of polymers were determined by gel permeation chromatography (g.p.c.) on a Tosoh HLC-803D with G2000H, G3000H and G5000H TSK gel columns and a differential refractometric detector in THF. The columns were calibrated with a set of monodisperse polystyrene standards

Monomers

2,4-Bis(N-octadecylanilino)-6-isopropenyl-1,3,5-triazine (BOIT). DAIT (15.2 g, 0.05 mol) was added to DMSO (300 ml) in the presence of sodium hydride (60% suspension in paraffin) (4.4 g, 0.11 mol) with stirring, and stirring was continued at 30°C for 2 h. Then, THF (100 ml) solution of octadecyl bromide (33.3 g, 0.1 mol) was added dropwise and stirred at 40°C for 24 h. The precipitated solid was filtered, and washed with water

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and methanol. The product was recrystallized three times from acetone: yield 31.1 g (77%), m.p. 57°C. Elemental analysis: calculated for $C_{54}H_{89}N_5$, C 80.24%, H 11.10%, N 8.66%; found, C 80.17%, H 11.39%, N 8.43%. ^1H n.m.r. ($CDCl_3$), δ (ppm) 0.88 (t, 6H, CH_3), 1.24 (m, 64H, $C_{16}H_{32}$), 1.93 (s, 3H, CH_3), 3.85 (t, 4H, N–CH_2), 5.30 (br s, 1H, CH), 6.20 (br s, 1H, CH), 7.30 (s, 10H, C_6H_5).

2,4-Bis(N-*ethylanilino)-6-isopropenyl-1,3,5-triazine* (*BEIT*). BEIT was synthesized by the reaction of DAIT with ethyl iodide similarly to the synthesis of BOIT. The reaction mixture was poured into a large excess of water to precipitate the solid. The solid was filtered, and washed with water. The product was recrystallized twice from methanol: yield 13.1 g (73%), m.p. 57°C. Elemental analysis: calculated for $C_{22}H_{25}N_5$, C 73.51%, H 7.01%, N 19.48%; found, C 73.53%, H 6.88%, N 19.68%. ^1H n.m.r. ($CDCl_3$), δ (ppm) 1.17 (t, 6H, CH_3), 1.95 (s, 3H, CH_3), 3.94 (q, 4H, N–CH_2), 5.32 (br s, 1H, CH), 6.22 (br s, 1H, CH), 7.27 (s, 10H, C_6H_5).

Polymerization

Homopolymerization of isopropenyltriazines and copolymerization with St and MMA were carried out using azobisisobutyronitrile (AIBN) as the initiator in benzene at 60°C. The monomer and AIBN concentrations were 0.3–0.4 mol l^{-1} and 1.4–2.4 mmol l^{-1}, respectively. The required volumes of monomer and AIBN solutions were charged into polymerization tubes, followed by degassing via three alternate freeze–pump–thaw cycles. After sealing, the tubes were placed in a constant temperature bath for specified times. After removal from the bath, the polymers were precipitated in excess methanol for the polymerization of BEIT and in methanol–THF mixture for the polymerization of BOIT, filtered, dried *in vacuo* and weighed. The composition of the copolymer was calculated by the elemental analysis of carbon and nitrogen contents.

RESULTS AND DISCUSSION

Synthesis of monomers

We have already reported the synthesis of 2-amino-4-(N-alkylanilino)-6-isopropenyl-1,3,5-triazines by the reaction of 2-amino-4-anilino-6-isopropenyl-1,3,5-triazine (AAIT) with alkyl halides in the presence of sodium hydride in DMSO[16]. The reaction proceeded selectively through the anilide anion of AAIT, which could be followed by the n.m.r. measurements.

By analogy with the above reaction, BOIT was synthesized from DAIT with octadecyl bromide in the presence of sodium hydride in DMSO (*Figure 1*). BEIT was also synthesized from DAIT with ethyl iodide as the monomer. It was found that the reaction also occurred through the anilide anion of DAIT similarly to AAIT by ^1H n.m.r. measurements. The monomers could be readily prepared and were characterized by i.r., ^1H n.m.r. and elemental analysis.

Polymerization

Homopolymerizations of BEIT and BOIT were carried out using AIBN as the initiator in benzene at 60°C. The results are shown in *Table 1*. Colourless solid polymer was obtained for BEIT, whereas poly(BOIT) was rubber-like. The polymerization yield of BOIT was lower than that of BEIT as shown in *Table 1*. In our previous paper[16], we reported that the polymerization rate for 2-amino-4-(N-alkylanilino)-6-isopropenyl-1,3,5-triazines was independent of the alkyl chain length. In this work, the polymerization rate decreased on introduction of two long alkyl groups. This could be due to the steric hindrance caused by the two bulky long alkyl groups in the propagation reaction, because the difference in electronic effect between the ethyl and octadecyl group is negligibly small.

In addition, we reported previously that ceiling temperature (T_c) and heat of polymerization (ΔH_p) decrease with increasing alkyl chain length for 2-amino-4-(N-alkylanilino)-6-isopropenyl-1,3,5-triazines[19]. This could be caused by steric hindrance of the long alkyl group in the polymer side chain. The T_c of the monomer containing hexadecyl group was 130°C in bulk. A lower T_c is expected for BOIT, because the steric hindrance of two long alkyl groups in BOIT is larger than that of the single long alkyl group in the previous monomer. Therefore, the low polymerization yield might be due to the limitation of polymerization by equilibrium monomer concentration in the present polymerization conditions (0.3 mol l^{-1}, 60°C).

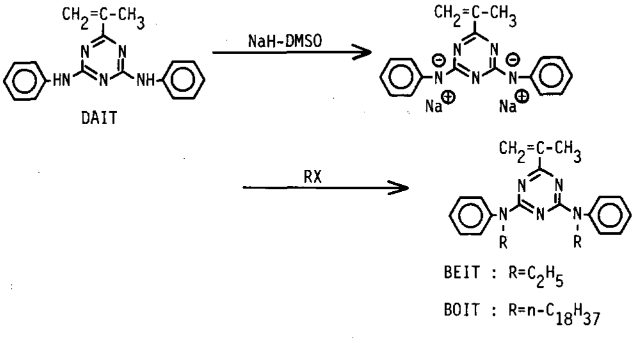

Figure 1 Synthesis of isopropenyl-1,3,5-triazines

Table 1 Homopolymerization of BEIT and BOIT[a]

Monomer	$[M]_0$ (mol l^{-1})	Time (h)	Yield (%)	η_{sp}/c[b] (dl g^{-1})	M_n[c] $\times 10^{-4}$	M_w[c] $\times 10^{-4}$	T_g[d] (°C)
BEIT	0.3	20	34.9	0.17	4.0	9.7	152
	0.4	20	41.1	0.18	4.7	10.1	152
BOIT	0.3	20	1.6	0.44	13.9	29.9	–
	0.3	50	18.0	0.52	14.7	38.2	–

[a] Polymerization conditions: [AIBN] = 2.4 mmol l^{-1} in benzene at 60°C
[b] $c = 0.2$ g dl^{-1} at 30°C in benzene
[c] Determined by g.p.c.
[d] Measured by d.s.c. at a heating rate of 20°C min^{-1}

The glass transition temperature (T_g) of the polymer was determined by d.s.c. The T_g of poly(BEIT), which was 152°C, is lower than that of poly(DAIT) ($T_g = 188°C$[18]). This could be attributed to the disappearance of the ability to hydrogen bond with displacement from hydrogen to ethyl group. The T_g of poly(BOIT) is below room temperature and could not be detected in d.s.c. curves. The introduction of two long alkyl groups in the monomer unit brings about a significant decrease in T_g of the polymer owing to internal plasticization.

The results of solubility for the homopolymers are given in *Table 2* together with the result of poly(DAIT). Poly(DAIT) was soluble only in polar solvents, while poly(BEIT) was soluble not only in polar solvents but also in non-polar solvents such as cyclohexane, benzene and toluene. On the other hand, poly(BOIT) was insoluble in dipolar aprotic solvents, and soluble in weak polar solvents.

Table 2 Solubility of homopolymers[a]

Solvent	Poly(DAIT)	Poly(BEIT)	Poly(BOIT)
Cyclohexane	−	+	+
Benzene	−	++	++
Toluene	−	++	++
Chloroform	±	++	++
Tetrahydrofuran	±	++	++
Ethyl acetate	±	++	−
m-Cresol	+	++	+
Pyridine	++	++	++
Dimethylformamide	++	++	−
Dimethylsulphoxide	++	±	−
Formic acid	±	++	−
Sulphuric acid	±	++	−

[a] Solubility: (++) soluble at room temperature
(+) soluble on heating
(±) partially soluble or swelling
(−) insoluble

Copolymerizations of the present monomers with styrene (St) and methyl methacrylate (MMA) were carried out in benzene at 60°C. The results are given in *Table 3*. The copolymer composition was calculated from the carbon/nitrogen ratio in the elemental analysis. The monomer reactivity ratios were determined by the method of Kelen and Tüdös[20]. The values of r_1 and r_2 are listed in *Table 4* together with $1/r_1$, which indicates the monomer reactivity. The reactivity ratios of DAIT are also listed in *Table 4*, which were estimated by copolymerization in DMSO[18]. Because the reactivity of isopropenyltriazines was influenced by the polymerization solvent as described previously[16,17], the comparison of the reactivity for DAIT with those for the present monomers would involve not only the substituent effect but also the solvent effect.

A significant decrease in $1/r_1$ was observed for BOIT compared with BEIT in the copolymerization with both comonomers. In our previous paper[17], we reported that the monomer reactivity was independent of the alkyl chain length in the copolymerization of 2-amino-4-(*N*-alkylanilino)-6-isopropenyl-1,3,5-triazines. Similar results for alkyl methacrylates have been observed by Otsu *et al.*[21] and Ito *et al.*[22]. In contrast to the previous reports, an effect of alkyl chain length on monomer reactivity was observed in this work. This could be due to the steric hindrance caused by the two bulkier long alkyl groups in the addition of propagating radical to BOIT. The r_2 value also decreased, which could be due to the decrease in the rate constant for addition of BOIT radical to BOIT (k_{22}) by considering that the homopolymerization rate of

Table 3 Copolymerization of BEIT or BOIT with styrene and methyl methacrylate[a]

Monomer				Copolymer			
M_2	M_1	$[M_2]$ (mol%)	Time (h)	Yield (%)	M_2 content (mol%)	η_{sp}/c[b] (dl g^{-1})	T_g[c] (°C)
BEIT	St	88.7	1.0	3.7	79.3	0.21	136
		66.3	1.3	3.8	64.6	0.21	135
		49.6	2.1	4.5	56.3	0.17	130
		33.0	2.5	4.7	46.2	0.14	118
		16.5	5.5	7.6	31.8	0.13	112
BEIT	MMA	88.4	0.5	4.3	80.4	0.45	144
		65.6	0.6	5.8	62.0	0.43	139
		48.8	0.7	6.2	51.0	0.39	135
		32.3	0.8	7.4	42.1	0.39	122
BOIT	St	90.0	4.0	11.5	77.7	0.30	
		80.8	4.0	8.5	65.7	0.39	
		63.2	4.5	5.5	54.2	0.30	
		47.1	5.5	5.1	46.9	0.30	
		25.3	7.0	8.5	35.9	0.26	
		12.2	8.0	5.5	22.8	0.29	
		5.9	8.7	4.1	15.3	0.23	
BOIT	MMA	88.9	5.4	6.2	59.1	0.50	
		74.7	1.0	6.8	53.3	0.53	
		53.8	0.5	6.8	46.4	0.49	
		48.4	0.6	12.7	42.2	0.51	
		38.0	0.7	7.9	36.2	0.66	
		28.3	0.7	9.4	31.8	0.43	
		12.9	1.0	11.8	20.7	0.53	
		8.6	3.0	8.7	16.0	0.43	

[a] $[M_1]+[M_2]=0.3$–0.4 mol l^{-1}, [AIBN] = 1.4–2.4 mmol l^{-1} in bezene at 60°C
[b] $c=0.2$ g dl^{-1} at 30°C in benzene
[c] Measured by d.s.c. at a heating rate of 20°C min^{-1}

BOIT was lower than that of BEIT. Furthermore, the decrease in r_2 might be due to low T_c in a similar manner as the homopolymerization.

Alfrey–Prince Q and e values for these isopropenyl-1,3,5-triazines calculated from monomer reactivity ratios are also listed in *Table 4*. The 1,3,5-triazinyl group acts as an electron-withdrawing group because of the electron-attracting character of nitrogen atoms. Actually, it has been reported that the e value increases with increasing nitrogen atoms in heterocyclic vinyl monomers. For example, the values were -0.28 for 4-vinylpyridine, 0.45 for 4-vinylpyrimidine and 0.92 for 2,4-dimethyl-6-vinyl-1,3,5-triazine, respectively[23]. Thus, a positive e value can be expected for the present monomer. However, the e values for BEIT depend on comonomers, i.e. they are positive for copolymerization with St and negative for MMA. This behaviour is general for the copolymerization of isopropenyltriazines as described previously[24,25]. The calculation from the monomer reactivity ratios gives two sets of data for Q and e. The other Q and e values for BEIT were 17.51 and -2.37 for the copolymerization with St, and 4.05 and 1.80 for the copolymerization with MMA, respectively. If we adopt the positive values for the copolymerizations with both comonomers, the Q value seemed to be too large in the copolymerization with MMA and the difference in these e values is not small similar to the values in *Table 4*. Therefore, we adopted the values in *Table 4*. One reason why the e values depend on the comonomers might be that the electron density of isopropenyltriazines varies dynamically with the properties of the comonomer or attacking radical. As a result of this effect, it seems that e_2 shows a positive value for the copolymerization with St, which exhibits nucleophilicity as well as its radical, and shows a negative value for that with MMA, which is electrophilic. The Q and e values for BOIT vary compared with those for BEIT, because the copolymerization of BOIT involves the steric effect.

Table 4 Copolymerization parameters of BEIT and BOIT

M_2	M_1	r_1	r_2	$1/r_1$	Q_2	e_2
BEIT	St	0.20	0.43	5.0	1.43	0.77
	MMA	0.32	0.44	3.1	1.32	-1.00
BOIT	St	0.35	0.26	2.9	0.83	0.75
	MMA	0.49	0.11	2.0	0.76	-1.31
DAIT[a]	St	0.28	0.99	3.6	1.45	0.33
	MMA	0.28	0.56	3.6	1.56	-0.91

[a] 2,4-Dianilino-6-isopropenyl-1,3,5-triazine[18], copolymerization was carried out in DMSO

The T_g values of the copolymers from BEIT are shown in *Table 3*. The T_g values of the copolymers with both St and MMA increased with BEIT content in analogy with previous results for 2-amino-4-(*N*-alkylanilino)-6-isopropenyl-1,3,5-triazines whose alkyl groups were ethyl[26] and propyl[17].

Crystallization of alkyl side chains

The crystallization behaviour of alkyl side chains for the resulting comb-like polymers from BOIT was investigated by d.s.c. measurements. The polymer sample was first heated from -120 to $+100$°C, then cooled to -120°C and again heated to $+100$°C at a scanning rate of 10°C min^{-1} in each case. D.s.c. curves of the polymers are shown in *Figure 2*. Endothermic peaks for the heating processes and exothermic peaks for the cooling processes were observed in the range of about -50 to $+50$°C. All the copolymers from BOIT exhibited the same tendency. No appreciable peaks were found in this temperature region for the polymers from BEIT. On the basis of extensive studies on conventional comb-like polymers[2–9], the endothermic peaks should be ascribed to the melting of crystallized alkyl side chains, and the exothermic peaks should be ascribed to their crystallization. The transition temperatures determined from the peak tops in the d.s.c. curves are shown in *Table 5*, which gives the m.p. on first heating process T_{m1}, crystallization temperature T_{cr}, and m.p. on second heating process T_{m2}. *Table 5* also shows the heat of fusion on first heating process ΔH_{m1}, heat of crystallization ΔH_{cr} and heat of fusion on second heating process ΔH_{m2}, which were estimated from the d.s.c. peak areas. The numbers of crystallizing CH_2 groups in a side chain (N) were calculated by dividing ΔH_{m2} by 3.08 kJ mol^{-1} per CH_2, which is a reported value for hexagonal-packed n-alkanes[8]. The present polymers showed singlet i.r. absorption at 725 cm^{-1}, which is characteristic for hexagonal-packed alkyl groups[8]. Because the values of ΔH_{m2} have the same thermal

Table 5 Transition temperatures and heats of transition for copolymers of BOIT

Polymer	M_2 in copolymer (mol%)	Transition temperature (°C) T_{m1}	T_{cr}	T_{m2}	Heat of transition (kJ (M_2 unit)$^{-1}$ mol^{-1}) ΔH_{m1}	$-\Delta H_{cr}$	ΔH_{m2}	N[a]
Poly(BOIT)	100	10	-3	8	24.35	23.26	25.36	4.12
Poly(BOIT-*co*-St)	77.7	23	-1	20	21.51	28.83	28.58	4.64
	66.7	9, 59	-1	15	23.68	19.54	18.07	2.93
	63.8	10	-4	14	15.94	14.64	17.36	2.82
	46.1	7, 51	-7	13	16.19	16.53	16.53	2.68
	35.9	3, 56	-12	11	13.97	12.72	12.55	2.04
Poly(BOIT-*co*-MMA)	63.1	15, 62	-3	17	20.21	12.26	12.89	2.09
	59.1	9	-2	10	13.85	14.27	14.10	2.29
	53.3	9	-3	12	19.83	16.65	18.95	3.08
	42.2	5, 58	-7	5	15.44	11.51	11.97	1.94
	34.0	-3, 60	-13	-7	17.20	8.20	10.75	1.75
	28.1	-9, 60	-14	-12	10.50	9.12	7.95	1.29
	16.0	-16, 60	-25	-20	9.04	4.39	4.85	0.79

[a] Number of crystallizing CH_2 groups in side chain evaluated from ΔH_{m2}

history in the d.s.c. measurement, the numbers N were evaluated by the use of ΔH_{m2}. On the other hand, melting point and heat of fusion on the first heating process varied widely for the copolymers owing to differences in thermal history. Poly(BOIT-*co*-St) shows two endothermic peaks on the first heating process at 51 and 7°C, respectively (*Figure 2b*). Similar behaviour was observed for the copolymers having two T_{m1} values in *Table 5*. An endothermic peak at higher temperature would be due to the melting of crystals that formed on standing at room temperature after the polymerization, whereas a peak at lower temperature is based on the crystals formed during the cooling from room temperature to -100°C before the d.s.c. measurement. The ΔH_{m1} value was calculated from the sum of the two peak areas.

The T_{m2} and N values in *Table 5* are plotted in *Figures 3* and *4* against the composition of the copolymers. The previous results[17] for the polymers for 2-amino-4-(N-octadecylanilino)-6-isopropenyl-1,3,5-triazine (N18) are also displayed in both figures for comparison. Both T_{m2} and N for BOIT polymers are higher than those for N18 polymers in the whole composition region. This indicates that the crystallinity and the perfection of the crystals are increased by the introduction of two long alkyl groups into the monomer unit. This could be due to the increase in the concentration of the alkyl side chains in the polymers. On the other hand, it has been reported that the crystallization of alkyl side chains depends on the flexibility of the polymer main chain[5-7,15]. The T_g values of polymers from N18 were observed above the m.p. of the side chains, whereas T_gs are lower than room temperature for BOIT polymers whose glass transition probably occurs at the m.p. of the side-chain crystal in a similar manner as the conventional comb-like polymers. The flexible main chain of BOIT polymers would be favourable to side-chain crystallization. Consequently, the side-chain crystallization of

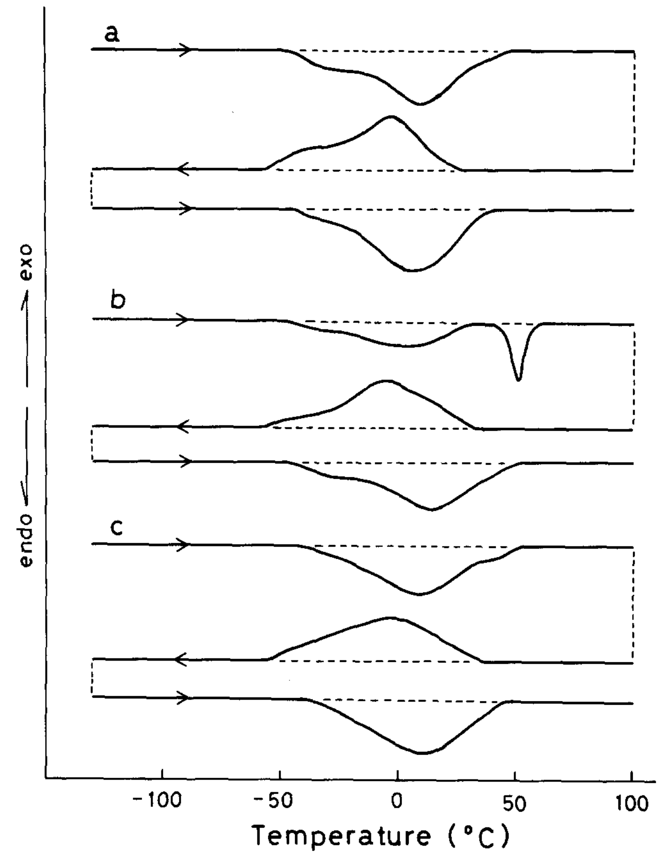

Figure 2 D.s.c. curves of (a) poly(BOIT), (b) poly(BOIT-*co*-St) ($M_2 = 46.1$ mol%) and (c) poly(BOIT-*co*-MMA) ($M_2 = 53.3$ mol%) at the scanning rate of 10°C $\min^{-1}$

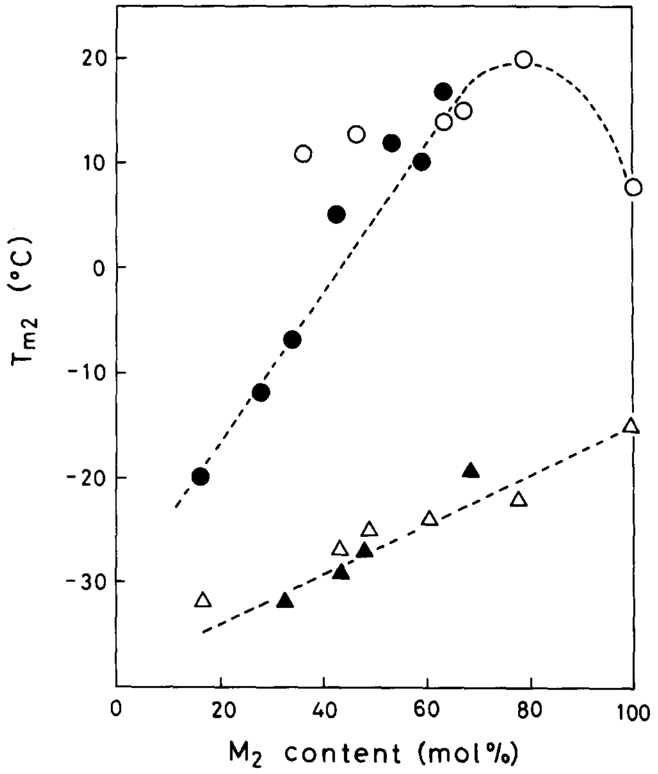

Figure 3 The relations between melting point of side chain (T_{m2}) and M_2 content in copolymer. Copolymer types are: (○), BOIT-St; (●), BOIT-MMA; (△), N18-St; (▲), N18-MMA

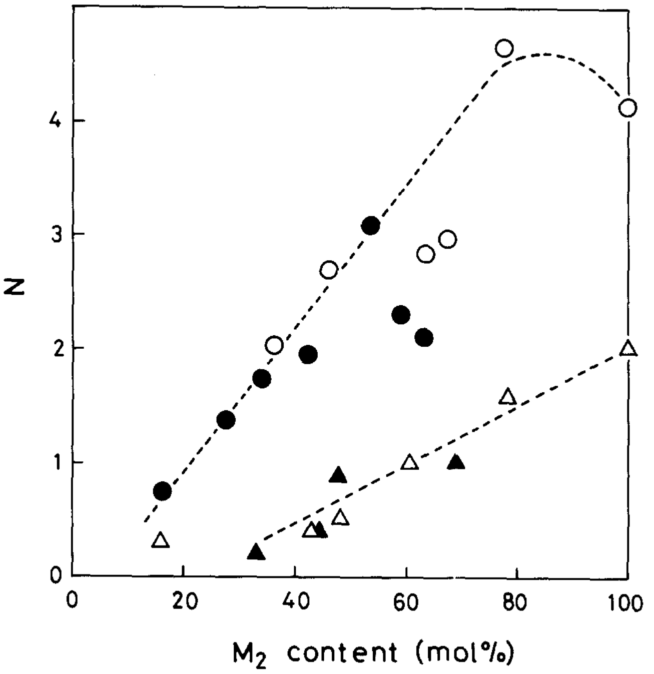

Figure 4 The relations between the number of crystallizing CH_2 groups in side chain (N) and M_2 content in the copolymer. Copolymer types are: (○), BOIT-St; (●), BOIT-MMA; (△), N18-St; (▲), N18-MMA

the present comb-like polymers would depend on the concentration of alkyl side chain and on the flexibility of the polymer main chain.

As can be seen in *Figures 3* and *4*, the values of T_{m2} and N increase with the M_2 content. This could be due to the increase in the concentration of the side chain as mentioned above. However, the values decreased for poly(BOIT). This trend could not be observed for poly(N18). The decrease in the values for homopolymer might be due to the limitation of segmental motion caused by crowded side chains. The comonomer unit might act as a spacer favourable to side-chain packing at high M_2 content in the copolymers.

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