Comb-Like Copolymers Obtained by Copolymerization of 2-Amino-4-(N-alkylanilino)-6-isopropenyl-1,3,5-triazines

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ABSTRACT: Copolymerizations of 2-amino-4-(N-alkylanilino)-6-isopropenyl-1,3,5-triazines with styrene, methyl methacrylate and methyl acrylate were carried out using azobisisobutyronitrile as an initiator. Alkyl groups were propyl, hexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, and docosyl. Copolymerization parameters (r_1, r_2, Q, and e) were determined for these monomers. No significant effect of alkyl chain length on the copolymrization parameters could be observed. Relationships between glass transition temperatures and composition of the copolymers were investigated. Crystallization exothermic and melting endothermic peaks due to the side-chains were observed in the DSC thermograms of the comb-like copolymers containing octadecyl and docosyl groups. The crystallinity of the side-chains decreased with increasing content of styrene or methyl methacrylate in the copolymers.
    KEY WORDS   Isopropenyltriazines / Long Alkyl Group / Copolymerization
            Parameters / Glass Transition Temperature / Comb-Like Copolymer /
            Side-Chain Crystallization /

Polymers containing long alkyl side-chains, so-called comb-like polymers, have attracted much attention due to specific properties such as side-chain crystallization,[1-3] peculiar mechanical properties,[3] ability of liquid crystal formation,[4-7] and formation of Langmuir-Blodgett film.[8] Furthermore, comb-like copolymers prepared by the copolymerization of long-chain monomers with common comonomers have been studied to improve solubility and to increase flexibility by internal plasticization.[9-15]

In a previous paper,[16] we reported the synthesis and polymerization of 2-amino-4-(N-n-alkylanilino)-6-isopropenyl-1,3,5-triazines, and found that long alkyl side-chains in the resulting comb-like polymers could be crystallized below the glass transition temperature (T_g) of the main-chain. On the other hand, we have studied substituent effects of isopropenyl-1,3,5-triazines on copolymerization behavior and property of the copolymers.[17-22] As a part of these studies, this paper deals with copolymerization parameters of isopropenyl-1,3,5-triazines containing long alkyl groups, and with the T_gs and the side-chain crystallization of the resulting comb-like copolymers.

The structures and abbreviations of isopropenyl-1,3,5-triazines used in this study are shown in Figure 1.

EXPERIMENTAL

Materials

2-Amino-4-(N-alkylanilino)-6-isopropenyl-1,3,5-triazines (N3, N6, N8, N10, N12, N14, N16, N18, and N22) were prepared from 2-amino-4-anilino-6-isopropenyl-1,3,5-triazine with alkyl bromides as described in the previous paper.[16] Styrene (St), methyl methacrylate (MMA), and methyl acrylate (MA) were commercially available and purified by usual

$CH_2=C-CH_3$
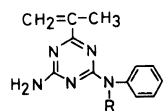
R = n-C_3H_7 (N3), n-C_6H_{13} (N6), n-C_8H_{17} (N8),
n-$C_{10}H_{21}$ (N10), n-$C_{12}H_{25}$ (N12), n-$C_{14}H_{29}$ (N14),
n-$C_{16}H_{33}$ (N16), n-$C_{18}H_{37}$ (N18), n-$C_{22}H_{45}$ (N22)

Figure 1. The structure and abbreviations of isopropenyl-1,3,5-triazines.

procedures. Dimethyl sulfoxide (DMSO), *N*,*N*-dimethylacetamide (DMAc), and benzene were distilled over calcium hydride under nitrogen.

Copolymerization

The copolymerizations of isopropenyl-1,3,5-triazines (M_2) with St, MMA, and MA (M_1) were carried out using azobisisobutyronitrile (AIBN) as an initiator in DMSO, DMAc, or benzene at 60°C. The monomers and AIBN concentrations were 0.15—0.40 mol l^{-1} and 1.4 mmol l^{-1}, respectively. The required volumes of monomers and AIBN solutions were charged into polymerization tubes and degassed by three alternate freeze-pump-thaw cycles. After being sealed, the tubes were placed in a constant temperature bath for specified times. The polymers were precipitated in excess methanol, filtered, dried *in vacuo*, and weighed. The composition of the copolymer was calculated by elemental analysis of carbon and nitrogen contents.

DSC Measurements

T_g of the copolymers was determined by differential scanning calorimetry (DSC) on a Rigaku-Denki DSC-8230 at a heating rate 20°C min^{-1}. DSC at low temperature region was measured from $-100°C$ to 100°C on a Rigaku-Denki Thermoflex with a low temperature unit at the heating and cooling rates 10°C min^{-1}.

RESULTS AND DISCUSSION

Copolymerization

Based on the solubility of the monomers, the copolymerizations were carried out in DMSO for N3, N6, N8, N10, and N12, in DMAc for N12, N14, N16, and N18, and in benzene for N22, respectively. All the monomers could be copolymerized with St, MMA, or MA (M_1), and white solid copolymers were obtained. In all cases the conversion of the copolymers was kept below 15%. 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.[23] Figure 2 shows the monomer–copolymer composition curves for the copolymerization of N3 (M_2) with St, MMA, and MA in DMSO. As can be seen in Figure 2, the plots fit the curves calculated from the reactivity ratios. The values of r_1 and r_2 are listed in Table I together with the previous values for the three monomers AAIT,[18] N2,[19] and N4.[19] In the case of the copolymerization of N3—N12 in DMSO, the monomer reactivity ratios did not change significantly. When the copolymerization solvent varied from DMSO to DMAc, the reactivity ratios changed, and especially r_2 values decreased. Homopolymerization rates for these monomers in DMAc were remarkably lower than those in DMSO as described previously.[16] The decrease in the r_2, which means a change in the copolymerization rate constant ratio k_{22}/k_{21}, is probably due to the decrease in k_{22}. Although the monomer reactivity ratios are generally said to be unaffected by changing solvent, some studies have revealed that the reactivity of polar monomers depends on the solvent.[24-28] Further, when the monomers have the ability of hydrogen bonding, such as acrylic acid,[29] acrylamide,[30,31] or 2-hydroxyethyl methacrylate,[32] strong influence of the solvent on the reactivity ratios is observed. The changes of reactivity have been explained by the monomer–monomer, monomer–solvent, and/or prop-
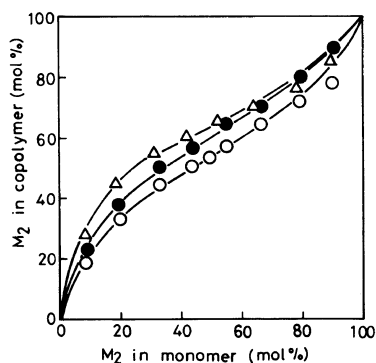
Figure 2. Monomer–copolymer composition curves for the copolymerization of N3 (M$_2$) with styrene (●), methyl methacrylate (○), and methyl acrylate (△) at 60°C in DMSO.

Table I. Copolymerization parameters

M$_2$	Solvent	M$_1$	r_1	r_2	Q_2	e_2
AAIT[a]	DMSO	St	0.39	0.78	1.07	0.29
		MMA	0.45	0.56	1.03	−0.77
		MA	0.14	1.55	1.43	−0.64
N2[b]	DMSO	St	0.24	0.83	1.15	0.47
		MMA	0.34	0.51	1.28	−0.92
		MA	0.08	1.13	2.07	−0.95
N3	DMSO	St	0.23	0.85	1.56	0.48
		MMA	0.32	0.56	1.37	−0.91
		MA	0.12	0.89	1.43	−0.90
N4[c]	DMSO	St	0.25	0.76	1.43	0.49
		MMA	0.33	0.45	1.29	−0.98
		MA	0.10	1.25	1.77	−0.84
N6	DMSO	St	0.24	1.01	1.61	0.39
		MMA	0.27	0.65	1.62	−0.92
		MA	0.11	0.99	1.56	−0.89
N8	DMSO	St	0.22	0.90	1.64	0.47
		MMA	0.28	0.63	1.56	−0.92
		MA	0.13	1.15	1.41	−0.78
N10	DMSO	St	0.21	1.00	1.75	0.45
		MMA	0.30	0.63	1.47	−0.89
		MA	0.11	1.89	1.80	−0.65
N12	DMSO	St	0.17	1.12	2.10	0.49
		MMA	0.26	0.57	1.64	−0.98
	DMAc	St	0.26	0.51	1.23	0.62
		MMA	0.39	0.38	1.08	−0.98
		MA	0.16	0.98	1.16	−0.76
N14	DMAc	St	0.22	0.43	1.31	0.73
		MMA	0.39	0.25	1.02	−1.13
		MA	0.15	1.11	1.24	−0.74
N16	DMAc	St	0.29	0.58	1.18	0.54
		MMA	0.38	0.30	1.07	−1.07
		MA	0.16	0.70	1.08	−0.88
N18	DMAc	St	0.27	0.55	1.23	0.58
		MMA	0.35	0.35	1.18	−1.05
		MA	0.13	1.26	1.44	−0.75
N22	Benzene	St	0.20	0.55	1.53	0.69
		MMA	0.20	0.15	1.72	−1.46

[a] 2-Amino-4-anilino-6-isopropenyl-1,3,5-triazine.[18]

[b] 2-Amino-4-(N-ethylanilino)-6-isopropenyl-1,3,5-triazine.[19]

[c] 2-Amino-4-(N-butylanilino)-6-isopropenyl-1,3,5-triazine.[19]

agating radical–solvent interaction, or changes in local concentration caused by aggregation of hydrogen bonding monomers. Since isopropenyl-1,3,5-triazines are polar monomers and have the ability of hydrogen bonding, the solvent effect on the reactivity ratios would be caused by the same reasons described above.

Significant effect of alkyl chain length on the reactivity ratios could not be observed. Similar results for alkyl methacrylates have been observed by Otsu et al.[33] and Ito et al.[34] Because the alkyl group exists in a fairly distant position from the active site in isopropenyltriazines, the reactivity ratios should be independent of the alkyl chain length.

Alfrey–Price Q and e values for these isopropenyl-1,3,5-triazines calculated from monomer reactivity ratios are listed in Table I. Although the Q and e values depend on the solvent effect, they are not influenced by changing alkyl chain length. On the other hand, the e values depend on comonomers, that is, positive for the copolymerization with St and negative for MMA and MA. This is a behavior general for the copolymerization of isopropenyltriazines as described previously.[18,21]

Glass Transition Temperatures

We studied the glass transition temperature (T_g) of copolymers of isopropenyltriazines with St or MMA.[18–22] T_gs increased almost linearly with the content of isopropenyltriazines in the copolymers. In this study, effects of the alkyl group on the T_g of the copolymers were investigated. Figure 3 shows the relations between the T_g and composition for the copolymers of N3 with St, MMA, and MA.
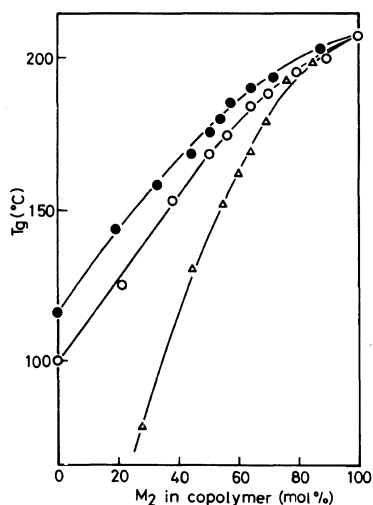
Figure 3. Relations between T_g and M_2 content in the copolymer of N3 (M_2) with styrene (◯), methyl methacrylate (●), and methyl acrylate (△).

Figure 4. Relations between T_g and M_2 content in the copolymer of N18 (M_2) with styrene (◯), methyl methacrylate (●), and methyl acrylate (△).

The T_g increases with the N3 content and reaches T_g of the homopolymer in a similar way to previous reports.[18-22] This result would be due to the strong intermolecular interactions of isopropenyltriazine units such as hydrogen bonding of amino group.

On the other hand, unique variation of T_g with composition is observed for the copolymers of N18 with St and MMA, as shown in Figure 4. The curves have the minima at the M_2 composition of around 20 mol% and have the maxima at around 70 mol%. Similar behavior was displayed for all the present copolymers containing above 6 carbon numbers of alkyl group. The minimum T_g around 20 mol% was lowered with increasing alkyl chain length of isopropenyltriazines. For N18 copolymers, the minimum T_gs are 80°C for N18-MMA copolymer and 65°C for N18-St copolymer, respectively, as shown in Figure 4. Because of internal plasticization caused by the introduction of small amount of long-chain monomer unit, the T_g of copolymer would be lowered than that of polySt or polyMMA until 20 mol% M_2 content. The internal plasticization effect would be enhanced with increasing
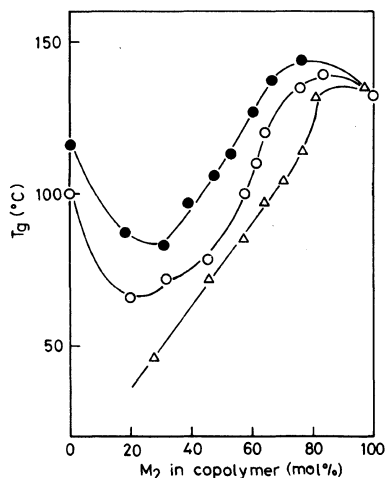
the alkyl chain length. The T_g rises with the M_2 content over 20 mol%, which is caused by the intermolecular interaction of isopropenyltriazine units. The lowering of the T_g, at the region of higher M_2 content near to homopolymer, might suggest the large blocking effect of a number of the long alkyl chains on the interaction. In other words, the comonomer unit might act as a spacer favorable to the interaction at M_2 content around 70 mol%.

Crystallization of Alkyl Side-Chains

The crystallization behavior of alkyl side-chains for the resulting comb-like copolymers was investigated by DSC measurement. The copolymer sample was first heated from $-100°C$ to $+100°C$, then cooled to $-100°C$, and again heated to $+100°C$, at a scanning rate of $10°C$ min^{-1} in each case. DSC curves of the copolymers of N22 with St and MMA are shown in Figure 5. Endothermic peaks on the heating processes and exothermic peaks on the cooling processes were observed in the range of about $-40°C$ to $+20°C$. Copolymers of N18 exhibited the same tendency. On the basis of extensive studies on conventional comb-like polymers,[3] the endothermic peaks

Table II. Transition temperatures and heats of transition for copolymers
of isopropenyltriazines

M_2	M_1	$\dfrac{dM_2}{\text{mol }\%}$	Transition temperature °C			Heat of transition kcal M_2 unit^{-1} mol^{-1}			N_{cr}[a]
			T_{m1}	T_{cr}	T_{m2}	ΔH_{m1}	$-\Delta H_{cr}$	ΔH_{m2}	
N18	St	78	-19	-33	-22	0.74	1.10	1.15	1.6
		61	-24	-34	-24	0.60	0.60	0.70	1.0
		49	-41	-34	-25	0.45	0.35	0.38	0.5
		44	-30	-37	-27	0.39	0.28	0.28	0.4
		17	-33	-50	-32	0.16	0.18	0.20	0.3
	MMA	69	-19	-24	-19	0.53	0.66	0.73	1.0
		48	-22	-35	-27	0.47	0.61	0.64	0.9
		44	-26	-39	-29	0.31	0.26	0.30	0.4
		33	-29	-39	-32	0.28	0.17	0.15	0.2
N22	St	62	1	-6	0	1.54	1.65	1.55	2.1
		58	-5	-14	-6	0.91	1.15	1.35	1.8
		42	-13	-19	-17	1.11	0.95	1.02	1.4
		28	-35	-77	-34	0.22	0.37	0.36	0.5
	MMA	76	9	1	8	2.05	2.59	2.61	3.6
		60	4	0	3	1.91	1.79	2.14	2.9
		51	2	-5	1	1.92	1.66	1.96	2.7
		42	-9	-18	-9	1.27	1.46	1.53	2.1
		19	-34	-74	-34	0.90	0.89	0.88	1.2

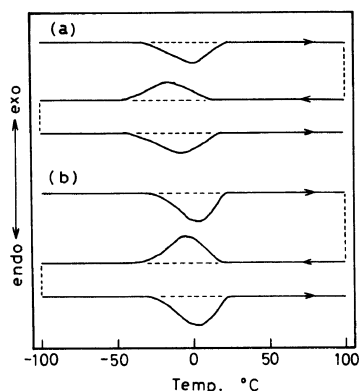[a] Number of crystallizing CH_2 groups in the side-chain.

Figure 5. DSC curves for copolymers of N22 (M_2) at the scanning rate of 10°C min^{-1}. (a) Copolymer with styrene ($dM_2 = 58$ mol%); (b) copolymer with methyl methacrylate ($dM_2 = 60$ mol%).

should be ascribed to the melting of crystallized alkyl side-chains, and the exothermic peaks should be ascribed to their crystallization. On the other hand, the endothermic and exothermic peaks were rarely found at this temperature region for the copolymers having alkyl side-chains up to 16 carbon numbers, although the side-chains could be crystallized for homopolymers having above 14 carbon numbers as described in the pervious paper.[16]

The transition temperatures determined from the peak tops in the DSC curves are shown in Table II, which give the melting point on the first heating process T_{m1}, crystallization temperature T_{cr}, and melting point on the second heating process T_{m2}. Table II 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}, as estimated from the DSC peak areas.

It is well known that the alkyl side-chains of conventional comb-like polymers crystallize in hexagonal form.[3] Assuming that the alkyl
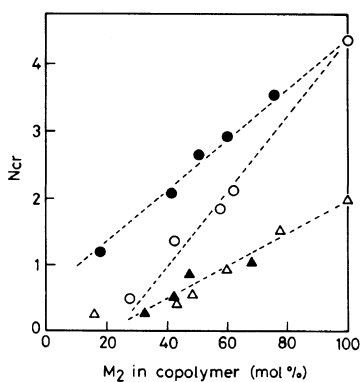
Figure 6. Relations between the number of crystallizing CH$_2$ groups in side-chain (N_{cr}) and M$_2$ content in the copolymer. Copolymer types are: △, N18-St; ▲, N18-MMA; ○, N22-St; ●, N22-MMA.

side-chains of the present copolymers crystallize to the hexagonal form, the numbers of crystallizing CH$_2$ groups (N_{cr}) were calculated from ΔH_{m2} on the basis of the heat of fusion of *n*-alkanes in the hexagonal packing (735 cal mol^{-1} CH$_2^{-1}$)[2]. Because of the same thermal history in the DSC measurement, the N_{cr} numbers were evaluated by the use of the ΔH_{m2}. The N_{cr} numbers are shown in Table II.

The N_{cr} numbers in Table II are plotted in Figure 6 against the composition of the copolymers. The N_{cr} numbers decrease with decreasing the M$_2$ content and the length of alkyl side-chain of the copolymers. Similar decreases are also observed in the melting points in Table II. These results indicate that the crystallinity and the perfection of the crystals depend on the concentration and the length of the alkyl side-chain in the copolymers.

Jordan *et al.* reported that the N_{cr} numbers of comb-like copolymers at the fraction of 50 mol% were 9.1 for octadecyl acrylate (OA)-MA, 5.1 for OA-MMA, and 5.7 for OA-acrylonitrile, respectively.[11] Hirabayashi *et al.* found the values of alternating comb-like copolymers to be 5.0 for OA-St, 2.7 for octadecyl methacrylate (OMA)-St, and 2.6 for OA-α-methylstyrene, respectively.[15] The copoylmers in this work gave N_{cr} smaller than those

of the conventional comb-like copolymers. In the conventional comb-like copolymers, it has been reported that the crystallization of alkyl side-chains is dependent on the flexibility of the polymer main-chain.[11-13,15] The glass transition of the conventional comb-like copolymers was observed at the melting point of the side-chains crystal. Therefore, the main-chain would be flexible enough to allow side-chain packing. However, T_gs of the present copolymers are higher than the melting points of the side-chains, and the side-chains crystallized below the T_g of the main-chain. Consequently, the less flexible main-chain of the present copolymers would prevent the side-chains crystallization and would give the smaller N_{cr} numbers.

Figure 6 also shows that the N_{cr} numbers of N22 copolymers are lowered by changes in comonomer from MMA to St. This is independent of their flexibility, because the copolymers of MMA exhibit higher T_g rather than the copolymers of St. This might be due to the compatibility of long alkyl group with phenyl group in St unit, which is based on the lipophilic property of the both groups. The alkyl side-chain packing would be prevented by the St unit as a result of compatibility.

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