Syntheses and Thermostabilities of *N*-Substituted Maleimide Copolymers. IV. Terpolymers Obtained from *N*-Cyclohexylmaleimide, Styrene and Acrylonitrile

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Abstract

In order to improve the thermostabilities of copolymers obtained from acrylonitrile (AN) and styrene (ST), so called AS resin, terpolymerization of *N*-cyclohexylmaleimide (CHMI) was achieved with ST and AN in the presence of radical initiator in benzene at 60 ℃. The obtained terpolymer had much better thermostabilities than the general AS resin. Weight loss and glass transition temperatures (T_g) of the terpolymers were 10 to 30 ℃ higher than those of general AS resin. Number-average molecular weights and polydispersity of terpolymers were 1.7×10^5 to 3.4×10^5 and 1.7 to 2.3, respectively.

1. Introduction

Polystyrene [poly(ST)] is generally known to be brittle and lacking in nature of strike¹⁾. In order to improve the defect, ST is copolymerized with acrylonitrile (AN). The obtained copolymer is the well-known "AS resin", which is prepared from 75 wt% of ST and 25 wt% of AN, and now used as the molding. Thermal property of AS resin is as follows : Bicat softening point (T_g) = 102 ℃ ; the softening point of the film (T_m) : 80-105 ℃ ¹⁾. The improval of the thermal stabilities of AS resin has been required. The most important characteristic of AS resin is transparent nature. The nature remains unchanged as it is, only the thermostabilities should be modified. There have been some reports on thermally stable AS resins, most of them were patents²⁾.

Lately *N*-substituted maleimide was found to be available for the thermal stability of the common vinyl polymers³⁾⁻⁵⁾. That is, thermostabilities of common vinyl polymers, especially of poly(ST), poly(methyl methacrylate) (MMA) and poly(vinyl acetate) (VAC) increased in cases of the polymers containing above 10 % of *N*-substituted maleimide³⁾⁻⁵⁾. In this article, solution terpolymerizations of ST, AN and *N*-cyclohexylmaleimide (CHMI) were carried out in benzene at 60 ℃. Polymerizabilities and thermal stability of terpolymers obtained were investigated. In addition, films of the terpolymer were prepared and their Bicat softening points were also determined.

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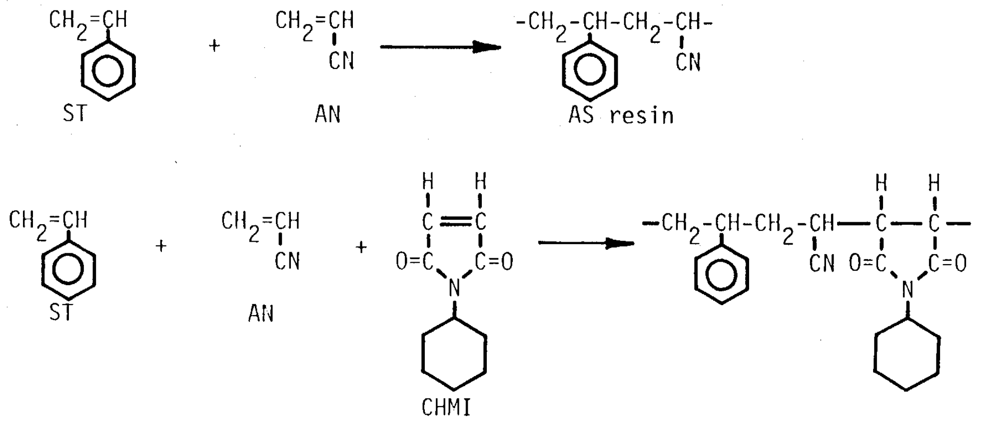

Scheme 1

2. Experimental

2.1 *Materials*

CHMI monomer was supplied from Nippon Oil & Fats Co., Ltd. CHMI was purified from ethanol/water (80vol/20vol) ; mp 88-89 ℃, colorless needles[3,6]. ST, AN, 2.2'-azobisisobutyronitrile (AIBN) and solvents were purified by the usual methods. Commerical methanol was used as a precipitant without further purification.

2.2 *Terpolymerization*

Terpolymerizations of CHMI, ST and AN were performed in the presence of AIBN as an initiator in benzene in a sealed glass tube at 60 ℃. After polymerization for a given time, the tube was opened, and the contents were poured into a large amount of methanol to precipitate the polymer, using the same techniques as described in previous papers[3~5]. The concentration of CHMI content was calculated from values of oxygen analysis.

2.3 *Measurements*

Molecular weights of the polymers were measured by gel permeation chromatographic (GPC) analysis by using the same techniques as reported previously[3]. Thermal gravimetric (TG) and differencial scanning calorimetric (DSC) analysis were done with the same instruments as reported previously[3]. Thermal mechanical analysis (TMA) was achieved with a Rigaku TMA apparatus, using a film of polymer as a sample. The film was prepared from a tetrahydrofuran (THF) solution of polymer.

3. Results and Discussion

3.1 *Terpolymerization*

An objective of this study is that the thermal property of actual AS resin should be improved. Accordingly, a ST/AN ratio in the monomer feed was 75/25 (wt/wt), whose value was actually taken in the industrial production, and a small amount of

Table 1 Terpolymerization of ST, AN, and CHMI in Benzene at 60 ℃[a]

run	ST[b]	AN[b]	CHMI in monomer feeds	Yield	CHMI in terpolymer[d]	$\overline{Mn}$	$\overline{Mw}/\overline{Mn}$
	mmol	mmol	mmol [mol%] (wt%)[c]	wt%	mol%	$\times 10^{-5}$	
0	0	2.00	0 [0] (0.0)	100	–	3.5	13.0
1	14.4	9.56	0 [0] (0.0)	51	–	1.7	2.1
2	14.4	9.46	0.09 [0.04] (0.5)	52	1.0	2.2	2.1
3	14.4	9.59	0.12 [0.48] (1.0)	53	1.7	1.8	2.0
4	14.4	9.42	0.29 [1.20] (2.5)	54	2.0	1.7	2.0
5	14.4	9.42	0.55 [2.26] (4.7)	58	2.7	2.0	2.3
6	14.4	9.55	0.83 [3.38] (7.0)	59	8.7	2.0	1.7
7	14.4	9.50	1.14 [4.55] (9.2)	66	12.2	2.2	2.4
8	14.4	9.52	1.66 [6.49] (13.0)	70	14.2	3.4	1.8
9	14.4	9.52	2.27 [8.67] (16.9)	75	17.2	3.3	1.7

[a] [AIBN] = 1.0×10^{-2} mol/L ; benzene = 2mL ; polymerization time = 17h.

[b] ST/AN = ca.75/25(wt/wt).

[c] wt% ; CHMI/(ST+AN+CHMI) × 100.

[d] Calculated from oxygen analysis ; error = 1.7mol%

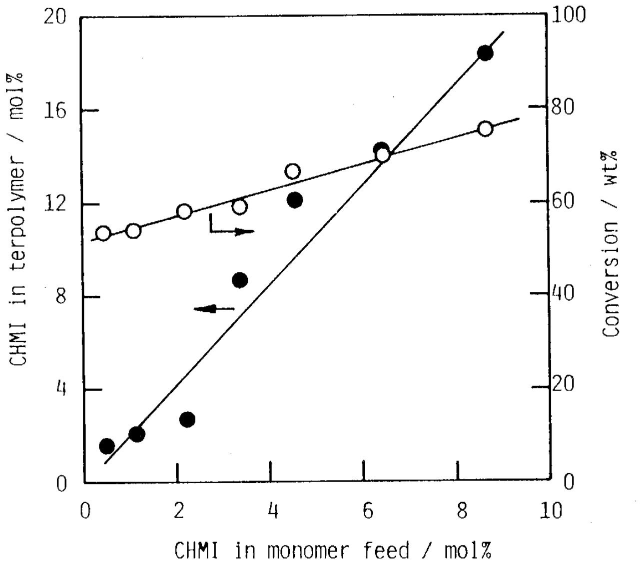

Fig. 1 Relationships between CHMI (mol%) in monomer feeds and (●) CHMI content (mol%) in terpolymer, and (○) yields (wt%) of terpolymer.

CHMI was added to the mixture. Results of terpolymerization are summarized in Table 1. Polymerizations were proceeded homogeneously throughout (run 1~9). However, homopolymerization of AN was proceeded heterogeneously ; that is, a part of polymers precipitated in benzene (run 0). The viscosities of the solution in all systems became extremely high with the elapse of time. Yields of polymers and contents of CHMI in the terpolymer linearly enhanced as the concentration of CHMI in the monomer feeds increased, as shown in Fig.1. The reason for the increase of

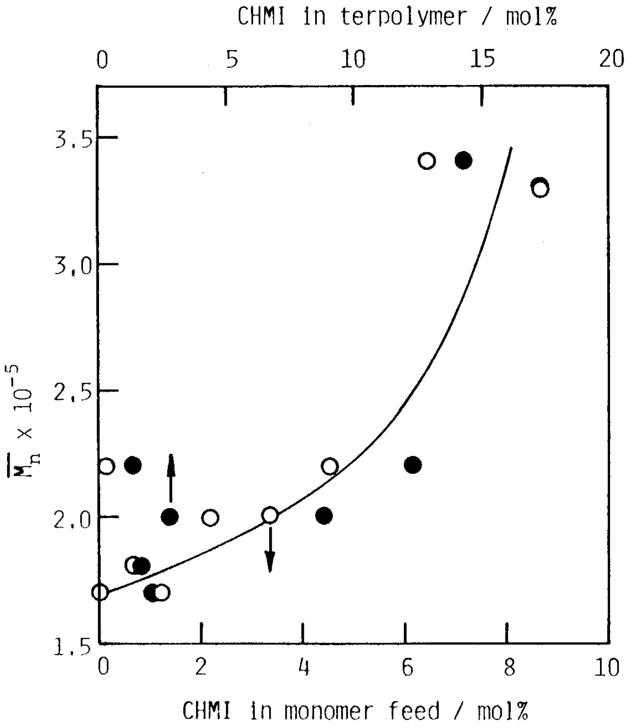

Fig. 2 Relations between number-average molecular weight (Mn) and (○) CHMI concentration (mol%) in monomer feeds, and (●) CHMI in terpolymer.

polymer yields and contents of CHMI in polymers would be attributable to the high reactivity of CHMI with ST. That is, CHMI has electrophilic nature because of e= 1.50, Q=0.5[6] and ST has nucleophilic one ; e=−0.8[7]. Accordingly, the reactivity was thought to be very high because of the electrostatic force of attraction between CHMI and ST. Thus terpolymerizability would rise. Fig.2 shows that relationships between the number-average molecular weight ($\overline{Mn}$) of terpolymers and the concentration (mol%) of CHMI in monomer feeds and in terpolymers. The molecular weights were 1.7×10^5 to 3.4×10^5. The molecular weights also rose with increasing the contents of CHMI in monomer feeds. The reason for this would be also ascribed to the high reactivity between ST and CHMI, described above. The obtained polymers were white powders, and soluble in such organic solvents as tetrahydrofuran (THF), benzene, toluene, chloroform, dioxane, dimethylformamide, dimethylsulfoxide. The films of polymers could be prepared from treatment of the THF solution. They were transparent and the thin was about 0.1 mm.

3.2 *Thermostabilities of terpolymers*

Typical TG and DSC curves for terpolymer (run 5) are shown in Fig.3. A TG curve indicated that an initial degradation of polymer was observed at about 294 ℃ .In the DSC curve, three endothermal peaks were observed based on a glass transition point (T_g), a melting point (T_m) (A in Fig.3), and a decomposition temperature of polymers (T_d) (B in Fig.3). TG and DSC curves for other terpolymers were similar patterns to those shown in Fig.3. However, T_g of polymers could not be observed

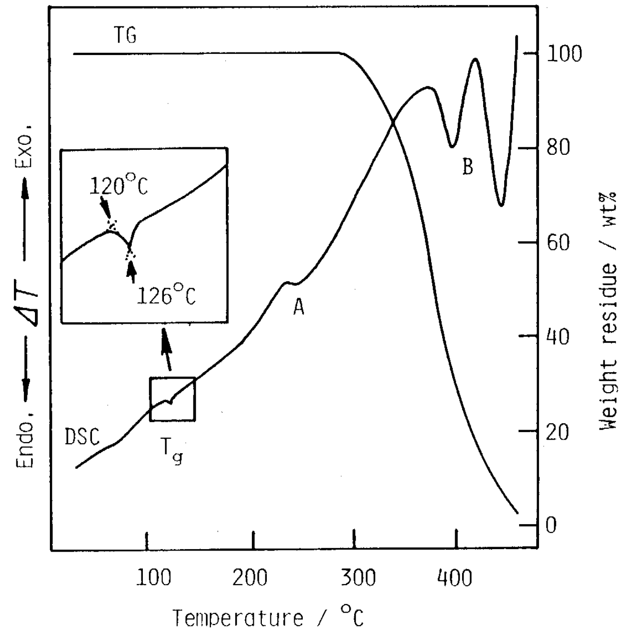

Fig. 3 TG and DSC curves for terpolymer [obtained from CHMI, ST, and AN (run 5)] at a heating rate of 10 ℃ min^{-1}in nitrogen.

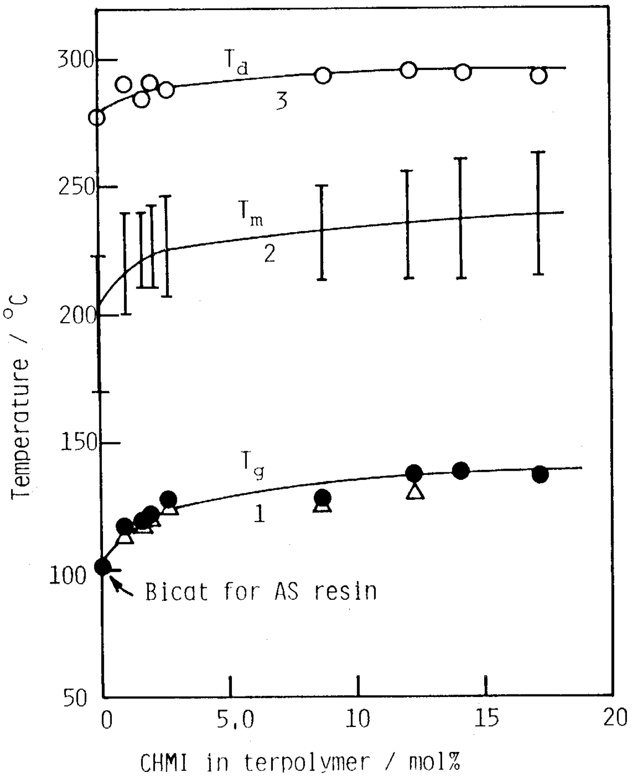

Fig. 4 Relationships between CHMI contents (mol%) in terpolymer and (1 ; △) T_g, (2) T_m, and (3) T_d determined from DSC curves, and (1 ; ●) T_g for the films of terpolymer obtained from TMA.

when the concentrations of CHMI in terpolymers were over 14.2 mol% (run 8 and 9). AS resin obtained from only ST and AN could not exhibit an appreciable T_g peak in the DSC curve.

An initial degradation temperature (T_d), T_m, and T_g, determined by DSC curves, are shown in Fig.4. As can be seen from Fig.4, the values of T_g (△) determined from DSC were exactly equal to those (●) measured by using TMA. A T_g obtained from TMA can be thought to agree with a Bicat softening point. T_g of the terpolymer was higher than the Bicat softening point of AS resin, i.e., 102 ℃. T_m and T_d of terpolymers obtained were also slightly higher than those of AS resin ($T_m = 170-223$ ℃ and $T_d = 278$ ℃ of the copolymer obtained from ST and AN [run 1]). In addition, T_g, T_d, and T_m slightly rose as the concentration of CHMI in terpolymer increased.

Thus the thermal stabilities of AS resin could increase by means of terpolymerization of ST, AN, and CHMI. The concentration of CHMI content were small amounts, i.e, 1 to 3 mol% in the terpolymer. The reason for the increase of the thermal stability of the terpolymer might be as follows: an AS resin, poly(ST-co-AN), could not contain polar functional groups like carbonyl one. CHMI has two carbonyl goups. Accordingly, the interactions among the molecules of ST, AN, and CHMI would play an important role in the thermal stability of AS resin.

In addition, transparent films could be prepared from the terpolymers.

4. Conclusion

1. Terpolymerization of CHMI, ST, and AN proceeded with relatively ease. The polymers containing CHMI were effectively obtained.
2. The transparent films could be prepared from the obtained terpolymers.
3. Thermostabilities of terpolymer obtained from CHMI, ST and AN were about 10 to 30 ℃ better than those of the general AS resin.

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