Copolymerization of 2-Bromomaleic Anhydride with Styrene and Its Dehydrobromination

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2-Bromomaleic anhydride (BrMAn) and styrene (St) were found to make a charge-transfer complex at a 1:1 ratio. The copolymerization followed the generalized mechanism for alternating copolymerization, and an alternating copolymer was obtained over a relatively wide feed composition range. The monomer reactivity ratios, r_{BrMAn} and r_{St}, were found to be 0 and 0.05, respectively, at 60 °C. The copoly(BrMAn/St) was dehydrobrominated by heating under reduced pressure and a polymer with a structure similar to the maleic anhydride moiety in the polymer chain was obtained. The dehydrobromination was completed by heating at 190 °C for 1 h.

Key words 2-bromomaleic anhydride; styrene; charge-transfer complex; copolymerization; dehydrobromination; formation constant

Maleic anhydride (MAn) acts as an electron acceptor and is easily polymerized with many monomers of electron donors. Copolymers of MAn and other monomers have been used for the immobilization of enzymes,[1,2] and as column packings for high-performance liquid chromatography.[3] In addition, SMANCS,[4] partially esterified copoly(MAn/styrene(St)) (SMA) conjugated with an antitumor protein neocarzinostatin (NCS) has been successfully used as a polymeric drug to increase the stability of the drug and reduce its susceptibility to hydrolysis in blood.

However, only a few studies have been carried out on the copolymerization of 2-substituted derivatives.[5] The copoly(2-chloromaleic anhydride (ClMAn)/St) was obtained as an alternating copolymer,[6] and on dehydrochlorination by heating the copoly(ClMAn/St) was found to have a structure similar to MAn moiety.[7] 2-Bromomaleic anhydride (BrMAn) has a bromine as a functional group. It is expected that the copolymer of BrMAn–other monomer more easily undergoes dehydrohalogenation by heating than that of ClMAn–other monomer because of the lower bond energy of C–Br than that of C–Cl.

In this report we studied the copolymerization of BrMAn with St and the dehydrobromination from the copolymer.

Results and Discussion

Formation of the Charge-Transfer (CT) Complex The absorption spectra of the BrMAn–St system and the individual components in benzene are shown in Fig. 1. The absorbance of the mixture system increased in comparison with the sum of the respective components, which suggested the formation of the CT complex. Figure 2 shows the continuous variation plots of the absorption of the CT complex. Maxima appeared at a 1 : 1 molar ratio of coordinated BrMAn to St. As the formation of the CT complex was suggested, the formation constant of the complex was determined by a spectrophotometric technique using the Benesi–Hildebrand equation[8] in Eq. 1,

$$\frac{[\mathrm{BrMAn}]\cdot l}{A_{\mathrm{CT}}}=\frac{1}{\varepsilon_{\mathrm{CT}}}+\frac{1}{K_{\mathrm{CT}}\cdot\varepsilon_{\mathrm{CT}}}\left(\frac{1}{[\mathrm{St}]}\right) \qquad (1)$$

where [BrMAn] and [St] are the concentration of BrMAn and St, respectively, l is the optical cell length, and A_{CT} and ε_{CT} are the absorption and the molar absorption coefficient of the complex. This equation is applicable to the system under conditions where [St]$\gg$[BrMAn]. The Benesi–Hildebrand plots for BrMAn and St at 350, 360, and 370 nm had a straight line relation, which suggested that the composition of the complex formed between

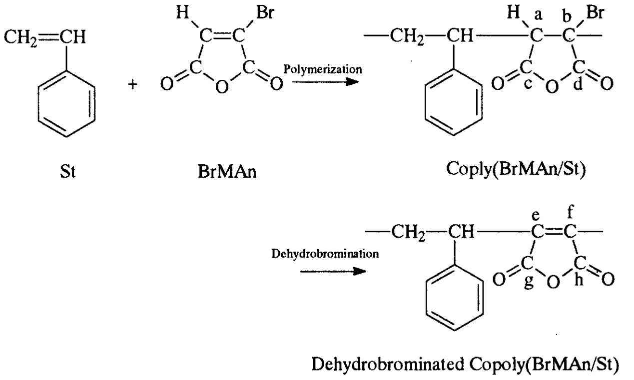

Chart 1

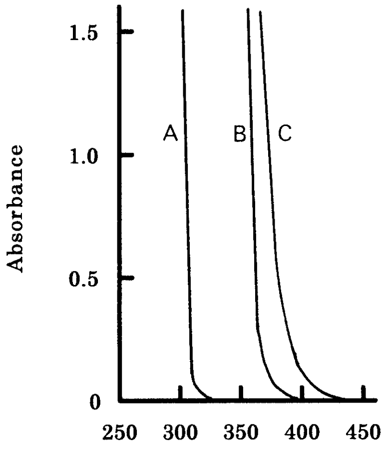

Fig. 1. Absorption Spectra for BrMAn–St System in Benzene at 25 °C

A, [St] = 0.25 (mol·dm^{-3}); B, [BrMAn] = 0.25 (mol·dm^{-3}); C, [St] = [BrMAn] = 0.25 (mol·dm^{-3}).

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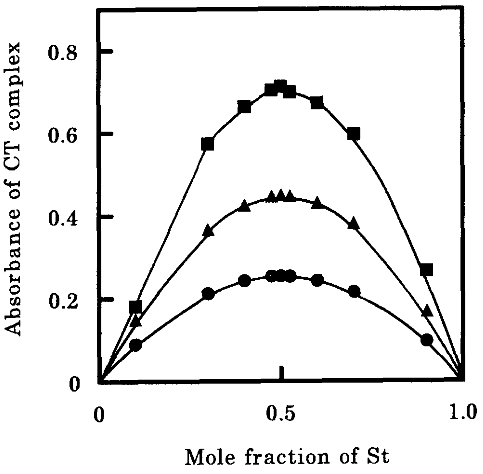

Fig. 2. Continuous Variation Plots of the CT Absorption for BrMAn–St System in Benzene at 25 °C

[BrMAn]+[St]=0.25 (mol·dm^{-3}). ■, 350 nm; ▲, 360 nm; ●, 370 nm.

Table 1. Formation Constants (K_{CT}) of CT Complex of St with BrMAn and ClMAn at 25 °C

	Solvent	K_{CT} (dm^{-3}·mol)
BrMAn	Benzene	0.00
BrMAn	Chloroform	0.10
BrMAn	Carbon tetrachloride	0.13
ClMAn	1,4-Dioxane	0.00[a]
ClMAn	Chloroform	0.115[a]

a) See reference 6.

BrMAn and St is 1 : 1. Table 1 presents the formation constants of the complex determined by the Benesi–Hildebrand plots in the various solvents. The K_{CT} value determined for BrMAn and St was nearly equal to that for ClMAn and St; thus BrMAn was found to act as an electron acceptor in the same manner as ClMAn.

Copolymerization of BrMAn with St Copolymerization of BrMAn with St was studied with benzoyl peroxide as initiator according to the method of Nagai *et al.*[6] The kinetic order regarding initiator concentration was 0.50 (50 °C) and the copolymerization rate was proportional to the BrMAn concentration at 60 °C. Consequently, the copolymerization of BrMAn with St was found to follow the generalized mechanism for alternating copolymerization proposed by Shirota and his colleagues.[9,10] The monomer CT complex played an important role in the initiation process but participated little in the propagation process.

Studies of the effect of the monomer feed composition on the copolymer composition showed that even if the monomer composition was changed, the polymer composition was maintained at an approximately equimolar level. The monomer reactivity ratios, r_{BrMAn} and r_{St} were determined to be 0 and 0.05, respectively, according to the Fineman–Ross method.[11] This proved that an alternating copolymer was obtained by the copolymerization of BrMAn with St.

Introduction of MAn Moiety by Dehydrobromination The copoly(BrMAn/St) for dehydrobromination was prepared in the same way as the copoly(ClMAn/St).[7] The molecular weight of the copoly(BrMAn/St) was lower than that (M_n, 3.35 × 10^3) of the copoly(ClMAn/St). This may be due to the steric hindrance of the bromine in a BrMAn molecule on the copolymerization.

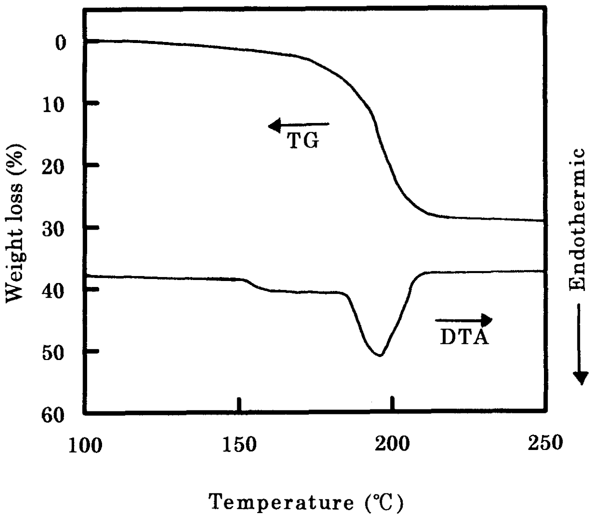

Fig. 3. TG–DTA Curves for Copoly(BrMAn/St)

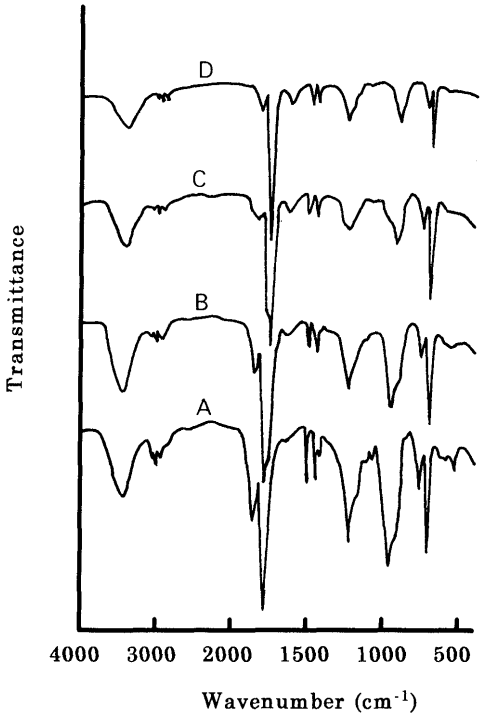

Fig. 4. Infrared Spectra of Copoly(BrMAn/St) and Dehydrobrominated Copoly(BrMAn/St) after Heating for 1 h

A, initial; B, 130 °C; C, 160 °C; D, 190 °C.

Figure 3 shows the thermal behavior of the copoly(BrMAn/St) examined by thermogranimetry (TG)–differential thermal analysis (DTA). The endothermic reaction was accompanied by a substantial weight loss due to dehydrobromination of the copoly(BrMAn/St) at approximately 190 °C. In the poly(ClMAn/St), a substantial weight loss was observed at 225 °C.[7] This difference is thought to be due to the lower bond energy of C–Br than of C–Cl. The weight loss by heating the copoly(BrMAn/St) from 100 to 250 °C corresponds to the calculated value (29%) of the complete removal of hydrogen bromide from the copolymer. An endothermic change of the copolymer in the DTA curve around 155 °C may be attributed to the glass transition.

Figure 4 shows the typical changes in IR spectra during the progress of dehydrobromination of the copoly(BrMAn/St) on heating for 1 h at 130, 160 and 190 °C. The initial copoly(BrMAn/St) (A) shows the characteristic absorption bands at 1795 and 1865 cm^{-1} for acid anhydride. When the polymer was heated at 190 °C (D), the absorption band for acid anhydride was found at 1760 and 1830 cm^{-1}, while the absorption band for C=C appeared at 1650 cm^{-1}. The bromine content in the copolymer after heating for 1 h at 130, 160 and 190 °C decreased to 21, 11, and 0%, respectively. The content of the double bond introduced in the copoly(BrMAn/St) by heating at 190 °C for 1 h was 4.6 mmol · g^{-1} and the content of carboxylic anhydride was 4.8 mmol · g^{-1}. These values are approximately in accordance with the calculated values (5.0 mmol · g^{-1}).

In conclusion, the interaction of BrMAn and St was found to make a CT complex at a 1 : 1 ratio. An alternating copolymer was obtained by copolymerization over a relatively wide feed composition range. The copoly(BrMAn/St) was easily dehydrobrominated by heating to give a polymer with a structure similar to the MAn moiety in the polymer chain.

Experimental

The IR spectra were recorded on a JASCO IR Report-810 spectrophotometer using KBr disks and the NMR spectra on a JNM-GSX400 FT NMR. The NMR sample solutions were prepared in $CDCl_3$ with a small amount of tetramethylsilane as an internal reference. The absorption spectra were obtained at 25 °C using a JASCO Ubest-30 spectrophotometer. The bromine content in the copolymer was determined by the oxygen combustion method. Thermal behavior (TG and DTA) were examined by TG–DTA (Rigaku) in a nitrogen atmosphere with an increase rate of 5 °C per minute. The molecular weight distributions[12,13] for the polymers were determined by gel permeation chromatography using a high performance liquid chromatography column (Asahipak GF-7M HQ, Asahi Chemical Industry, Co., Ltd.), tetrahydrofuran as the mobile phase at 25 °C, and standard polystyrenes.

Materials BrMAn (Aldrich Chemical Company Inc.) and St (Wako Pure Chemical Industries, Ltd.) were purified by distillation under reduced pressure. Benzene, chloroform and carbon tetrachloride were distilled before use. All other chemicals were of reagent grade.

Copolymerization of BrMAn with St and Its Dehydrobromination Copolymerization behavior of BrMAn with St was studied at 50 or 60 °C using benzoyl peroxide as an initiator in a glass tube (15 ml) under a nitrogen atmosphere in the dark according to the method of Nagai *et al.*[6] The copolymer yield was calculated based on the total monomers in the feed.

The copoly(BrMAn/St) for dehydrobromination was prepared as follows. BrMAn (17.7 g) and St (10.4 g) were copolymerized in the presence of 360 ml of benzene and 0.10 g of benzoyl peroxide at 80 °C for 2 h under a nitrogen atmosphere. After polymerization, the reaction mixture was cooled to room temperature and then added to *n*-hexane to obtain a precipitate. The mixture was centrifuged and the supernatant liquid was removed. The copolymer precipitate was then dissolved in 50 ml of benzene. The benzene solution was added to 400 ml of *n*-hexane to obtain a light yellow powdery precipitate. This was washed with *n*-hexane and dried *in vacuo* at 40 °C to give a constant weight. Eight grams of copolymer was obtained. The weight-average molecular weight (M_w), the number-average molecular weight (M_n), and the polydispersity (M_w/M_n) of copoly(BrMAn/St) were 1.90×10^3, 0.83×10^3, and 1.79, respectively. ^{13}C-NMR ($CDCl_3$) δ: a, 53.7 (CH); b, 59.3 (CBr); c, d, 166.8 or 167.1 (CO) (a—d: see Chart 1).

The copoly(BrMAn/St) was heated at various temperatures for 1 h to eliminate hydrogen bromide from the copolymer. After the dehydrobromination, the copolymer was dissolved in benzene and precipitated in a similar manner to that above. The double bond introduced and carboxylic anhydride were analyzed in the usual way.[14] M_w, M_n, and M_w/M_n of dehydrobrominated copoly(BrMAn/St) were 1.78×10^3, 1.10×10^3, and 1.61, respectively. ^{13}C-NMR ($CDCl_3$) δ: e, f, 137.0 or 145.1 (C=C); g, h, 164.5 (CO) (e—h: see Chart 1).

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