Dehydrochlorination of Copoly(styrene/2-chloromaleic anhydride)

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Synopsis. 2-Chloromaleic anhydride and styrene were copolymerized by solution polymerization. The copoly(styrene/2-chloromaleic anhydride) was dehydrochlorinated by heating under reduced pressure and a polymer having a structure similar to the maleic anhydride moiety in the polymer chain was obtained. The dehydrochlorination was completed by heating at 220 °C for 1 h.

Maleic anhydride forms donor–acceptor complexes with many compounds and is known to copolymerize with various other monomers.[1—7] On the other hand, only a few works have been undertaken on the copolymerization of 2-substituted maleic anhydride derivatives.[8—11] 2-Chloromaleic anhydride and styrene copolymerize to yield an alternating copolymer.[10] Polymers retaining maleic anhydride moiety in the polymer chain are expected to act as electron acceptors for donors such as styrene. Here we report that the copoly(styrene/2-chloromaleic anhydride) is easily dehydrochlorinated by heating under reduced pressure and as a result becomes a polymer having a structure similar to maleic anhydride.

Experimental

The IR spectra were recorded on a JASCO IR Report-100 spectrophotometer using KBr disks. The carbon and hydrogen contents of the polymers were determined at the Analytical Center, College of Science and Technology, Nihon University. Thermal behavior (TG and DTA) was examined by TG-DTA (Rigaku) in nitrogen atmosphere with an increasing rate of 5 °C per minute. The molecular weight distributions for the polymers were determined by gel permeation chromatography[12,13] using high performance liquid chromatography column (Asahipak GF-7M HQ, Asahi Chemical Industry, Co., Ltd.) and tetrahydrofuran as the mobile phase at 25 °C.

Materials. Styrene and 2-chloromaleic anhydride (Wako Pure Chemical Industries, Ltd.) were purified by distillation under reduced pressure. Benzene was distilled before use. Dioxane was purified by refluxing with sodium and then distilled. All other chemicals were of reagent grade.

Copoly(styrene/2-chloromaleic anhydride). 2-Chloromaleic anhydride (13.2 g) and styrene (10.4 g) were polymerized 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. The supernatant liquid of the reaction mixture was decanted off and the mass of copolymer stuck in the bottom of the reaction vessel was washed with 200 ml of benzene and the washing was discarded and then the copolymer was dissolved in 100 ml of hot dioxane. After the dioxane solution was cooled to room temperature, the dioxane solution was added to the mixture of 200 ml of benzene and 400 ml of hexane. The precipitated white solid was washed with hexane and dried in vacuo at 60 °C to give a constant weight. Yield (copolymer), 12 g. The weight-average molecular weight (M_w), the number-average molecular weight (M_n), and the polydispersity (M_w/M_n) of the copolymer were 2.78×10^4, 3.35×10^3, and 8.30, respectively.

Dehydrochlorination. The copoly(styrene/2-chloromaleic anhydride) was heated at various temperatures for a definite time under reduced pressure. After performing the dehydrochlorination, the copolymer was dissolved in dioxane and precipitated in a similar manner as described above. The chlorine content in the resulting polymer was determined by the oxygen combustion method. The double bond introduced and carboxylic anhydride were analyzed in the usual way.[14] M_w, M_n, and M_w/M_n of the dehydrochlorinated polymer were 2.63×10^4, 9.14×10^3, and 2.88, respectively.

Results and Discussion

The thermal behavior of copoly(styrene/2-chloromaleic anhydride) examined by TG-DTA is shown in Fig. 1. The endothermic reaction was accompanied by substantial weight loss due to dehydrochlorination of the copoly(styrene/2-chloromaleic anhydride) at around 225 °C. The weight loss corresponds to the calculated value (16%) of complete removal of hydrogen chloride from the copoly(styrene/2-chloromaleic anhydride). Taking into account the TG-DTA data, the copoly(styrene/2-chloromaleic anhydride) was heated at 170, 200, 210, and 220 °C under reduced pressure. The analytical data and weight loss of the polymer are shown in Table 1. The chlorine content in the copoly(styrene/2-chloromaleic anhydride) is in agreement with the calculated value based on the assumption that the copolymer is an alternating copolymer.

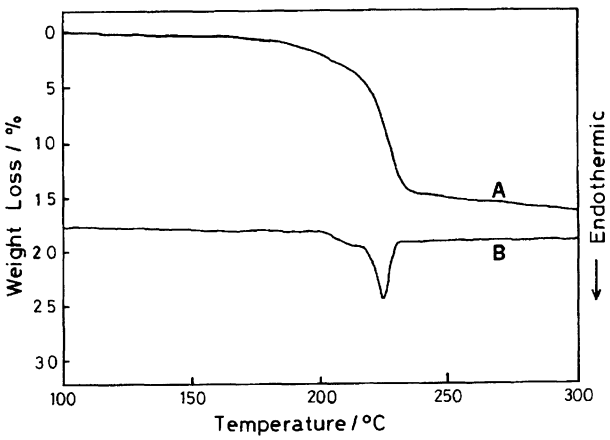

Fig. 1. TG(A)–DTA(B) curves for copoly(styrene/2-chloromaleic anhydride).

Table 1. Dehydrochlorination of Copoly(styrene/2-chloromaleic anhydride)[a)]

Condition	Elemental analysis			Weight loss
	C/%	H/%	Cl/%	%
—	59.7(60.9)	4.4(3.8)	15.0	—
170 °C, 1 h	62.1(62.7)	4.2(3.9)	12.6	4
200 °C, 1 h	66.1(65.9)	4.1(3.9)	8.2	10
210 °C, 1 h	69.6(69.2)	4.3(4.0)	3.8	14
210 °C, 3 h	71.3(71.7)	4.0(4.0)	0.4	16
220 °C, 1 h	72.4(72.0)	4.2(4.0)	0	16

a) Values in parentheses indicate the calculated value based on Cl content.

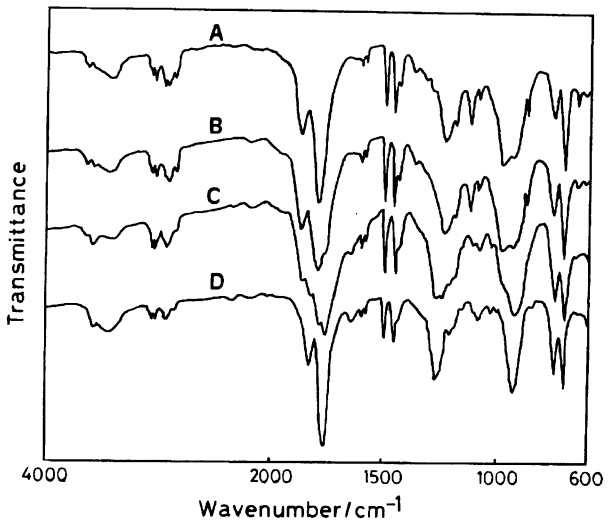

Fig. 2. Infrared spectra of polymers. A) Initial, B) heated to 170 °C, C) heated to 210 °C, D) heated to 220 °C.

The extent of dehydrochlorination is small when the copolymer is heated at 170 °C but is gradually increased with the increase in the heating temperature. The findings indicate that heating of the copolymer at 220 °C for 1 h is sufficient to remove hydrogen chloride from the copolymer. These behaviors are substantiated by the results shown in Fig. 1. The typical changes in IR spectra on the progress of dehydrochlorination of the polymer at 170, 210, 220 °C for 1 h are shown in Fig. 2. The initial copoly(styrene/2-chloromaleic anhydride) (A) shows the characteristic absorption bands at 1790 and 1865 cm^{-1} for acid anhydride and 650 cm^{-1} (C–Cl). When the polymer was heated at 220 °C (D), the absorption band for acid anhydride is found at 1760 and 1830 cm^{-1}, the absorption band for C=C appeared at 1650 cm^{-1} and C–Cl (650 cm^{-1}) disappeared. The polymers heated at 170 and 210 °C, B and C, showed intermediate absorption bands between polymer A and D. The content of the double bond introduced in the polymer by heating at 220 ° for 1 h was 4.8 mmol g^{-1} and the content of carboxylic anhydride was 4.9 mmol g^{-1}. These values are roughly in accordance with the calculated values (5.0 mmol g^{-1}).

In conclusion, the copoly(styrene/2-chloromaleic anhydride) was easily dehydrochlorinated only by heating to give a polymer having a structure similar to the maleic anhydride moiety in the polymer chain.

Interaction of substrate (electron donor) such as styrene with the dehydrochlorinated polymer is now under investigation.

References

1) P. D. Bartlett and K. Nozaki, *J. Am. Chem. Soc.*, **68**, 1495 (1946).
2) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **75**, 3776 (1953).
3) E. Tsuchida and T. Tomono, *Makromol. Chem.*, **141**, 265 (1971).
4) E. Tsuchida, T. Tomono, and H. Sano, *Makromol. Chem.*, **151**, 245 (1972).
5) K. Dodgson and J. R. Ebdon, *Eur. Polym. J.*, **13**, 791 (1977).
6) N. Ogawa, K. Honmyo, K. Harada, and A. Sugii, *J. Appl. Polym. Sci.*, **29**, 2851 (1984).
7) B. C. Trivedi and B. M. Culbertson, "Maleic Anhydride," Plenum, New York (1982), p. 307.
8) H. K. Hall, Jr., P. Nogues, J. W. Rhodes, R. C. Sentman, and M. Detar, *J. Org. Chem.*, **47**, 145 (1982).
9) K. Nagai and H. Yonezawa, *J. Polym. Sci., Polym. Lett. Ed.*, **21**, 115 (1983).
10) K. Nagai, K. Akiyama, and N. Kuramoto, *Makromol. Chem.*, **186**, 1855 (1985).
11) K. Inoue, H. Kaku, H. Hayashi, and T. Tanigaki, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 4231 (1989).
12) J. Cazes, *J. Chem. Educ.*, **43**, A625 (1966).
13) Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci., Polym. Lett. Ed.*, **5**, 753 (1967).
14) F. E. Critchfield, *Anal. Chem.*, **31**, 1406 (1959); N. D. Cheronis and T. S. Ma, "Organic Functional Group Analysis by Micro and Semimicro Methods," Interscience, New York (1964), p. 522.