Alternative Copolymerization of 2, 4-Hexadiene with Maleic Anhydride and Some Other Compounds

Masao Iwamoto and Sadao Yuguchi

Central Research Laboratories, Toyo Rayon Company, Ltd., Sonoyama, Otsu

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2, 4-Hexadiene is the simplest internal-conjugated diene; it is obtained by catalytic isomerization of 1, 4- or 1, 5-hexadiene. Our attempt to obtain the Diels-Alder adduct by reacting 2, 4-hexadiene, which was obtained by the isomerization of 1, *cis*-4-hexadiene, with maleic anhydride gave a result different from the literature.[1,2] An equimolar mixture of 2, 4-hexadiene and maleic anhydride was heated at 100°C for 300 min. A very viscous product was recovered; it was then coagulated by adding methanol and dried in a vacuum. The results of the reactions are shown in Table 1. The only product is a white powder which is readily soluble in ethyl acetate and an aqueous alkaline solution. A hard, transparent sheet was prepared by pressing the powder under 70—90 kg/cm^2 at 150°C. The characteristic absorption bands of the methyl group, of carbon-carbon unsaturation, and of the carbonyl group of acid anhydride was observed in the infrared spectrum (shown in Fig. 1A). The results of an elemental analysis of the products suggested that an alternating copolymerization took place.

Although the composition of the three geometrical isomers fluctuated as the isomerization conditions changed, the 2, 4-hexadiene used in this study had the composition: *trans, trans*-, 10%; *trans, cis*-, 60%; *cis, cis*-, 30%. It is considered that the *trans, cis* and *cis, cis* isomers are sterically hindered to form a cyclic adduct with maleic anhydride, since they must have a hydrocarbon group in the *cis* position. Therefore, in the same way as with *cis*-piperylene,[3] the sterically-hindered isomers of 2, 4-hexadiene display a tendency to form a polymeric substance with maleic anhydride instead of a ring-forming reaction product.

An essential difference of the reaction conditions, comparison with those in the literature, in which the crystalline adduct could be obtained, was the content of the sterically-hindered isomers of 2, 4-hexadiene. We could obtain needle crystals

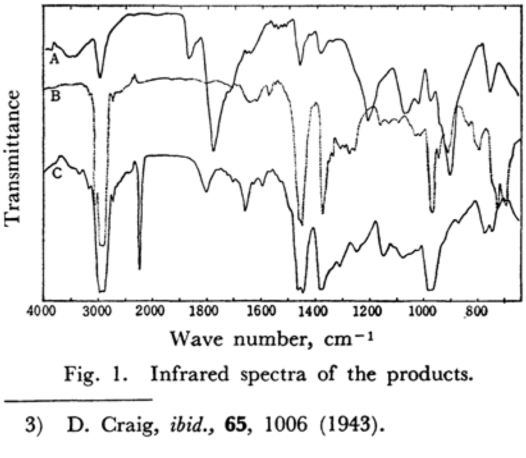

Fig. 1. Infrared spectra of the products.

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[1] A. L. Henne and A. Turk, *J. Am. Chem. Soc.*, **64**, 826 (1942).

[2] L. K. Montgomery, K. Schueller and P. D. Bartlett, *ibid.*, **86**, 622 (1964).

[3] D. Craig, *ibid.*, **65**, 1006 (1943).

Table 1. Copolymerization of 2, 4-hexadiene with maleic anhydride in ethyl acetate

Run No.		1	2	3	4	5	6
Ethyl acetate, m*l*		—	100	50	50	50	50
2, 4-Hexadiene, g		33	46.5	23.2	23.2	23.2	23.2
Maleic anhydride, g		40	50	25	25	25	25
Radical initiator, g		—	—	—	—	AIBN 0.5	BPO 0.5
Temperature, °C		100	40	90	80	95	80
Time, min		300	1440	35	35	35	15
Yield, g		71	76.9	5.8	1.2	40.3	35.7
Mp, °C		136—138	163—165	148—152	150—155	123—125	113—117
Elemental analysis, %	C		65.91	63.81		65.79	65.32
	H		6.94	6.84		7.02	6.78
	O		27.24	28.72		27.17	29.95

(mp 93°C) from a reaction of the 2, 4-hexadiene obtained by the isomerization of *trans*-rich 1, 4-hexadiene[4] with maleic anhydride, accompanying by the polymer. The infrared spectrum of the crystals was obviously different from the spectrum shown in Fig. 1A. The copolymerization can be explained in terms of the formation of an activated complex intermediate containing the diene and the anhydride, and its rapid polymerization. The radical mechanism has been assumed for the copolymerization of olefins and dienes with maleic anhydride.[5] The copolymerization in the presence of a radical initiator such as benzoyl peroxide (BPO) or α, α'-azobis(isobutyronitrile) (AIBN) took place rapidly (Table 1).

Copolymerizations of 2, 4-hexadiene with other polymerizable monomers were also possible. For example, by heating 2, 4-hexadiene with cyclopentadiene in an autoclave at 200—220°C, a gluey substance was formed. Its infrared spectrum is shown in Fig. 1B. A glassy polymer (Fig. 1C) with a low softening temperature was obtain by the copolymerization of 2, 4-hexadiene with acrylonitrile in the presence of AIBN. The results of the elemental analysis of the product were as follows:

Found: C, 79.2; H, 9.8; N, 10.8%. Calcd for $(C_9H_{13}N)_n$: C, 80.1; H, 9.6; N, 10.3%. These results suggest also an alternating copolymerization. The terpolymerization of a mixture of 23.4 g of 2, 4-hexadiene, 25 g of maleic anhydride, and 25 g of methyl acrylate was carried out for 60 min at 90°C in the presence of 0.5 g of AIBN. The yield of the powdery product (melting at 124—127°C) was 63.2 g. The results of the elemental analysis of the product were as follows: C, 63.49; H, 7.15; O, 28.55%. A film made from the terpolymer was more flexible than the film made from the 2, 4-hexadiene-maleic anhydride copolymer.

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[4] T. Alderson, E. L. Jenner and R. V. Lindsey, Jr., *ibid.*, **87**, 5638 (1965).

[5] Y. Tsuda, T. Sakai and T. Shinohara, IUPAC International Symposium on Macromolecular Chemistry, Tokyo-Kyoto (1966). Preprints No. 4-2-13.