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Alternate Copolymerization of Acrylonitrile and Isobutylene

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The polymerization of isobutylene and acrylonitrile was described in a patent,[1] in which copolymerization was carried out in the presence of $ZnCl_2$ as a complexing agent together with organic peroxide as an initiator, but the structure of the copolymer has not yet been established. Gaylord *et al.*[2] assumed the copolymer to be of an alternate structure from the fact that the copolymer is always of 1:1 composition irrespective of the variation of the composition of feed monomers, but no chemical evidence for the alternate structure was afforded.

Hirooka *et al.*[3] reported the preparation of 1 : 1 copolymer from acrylonitrile and α-olefin such as styrene and propylene and concluded the alternate structure by means of IR analysis. They found $AlEtCl_2$ to be a good complexing agent, which initiates polymerization without any initiator, but neither $AlEt_3$ nor $AlCl_3$ was effective.

We have made the 1 : 1 copolymer of isobutylene and acrylonitrile in good yield in a similar way to the patent except for using $AlCl_3$ and peroxide and have established the structure of the copolymer to be alternate.

The polymerization was carried out as follows. A 25 cc glass tube was charged with 2 cc of toluene, 0.5 mmol of benzoyl peroxide, 50 mmol of acrylonitrile containing 1 mmol of $AlCl_3$ and 50 mmol of isobutylene under nitrogen atmosphere at −78°C. Subsequently the tube was sealed and was subjected to polymerization at 25°C. After 20 hr, 0.256 g of white polymer was obtained. It was completely soluble in acetone and this fact indicates that the product is a copolymer since each homopolymer is insoluble in acetone. The polymer possesses an intrinsic viscosity of 0.15 d*l*/g at 30°C in chloroform and contains 52 mol% of acrylonitrile unit according to an elementary analysis.

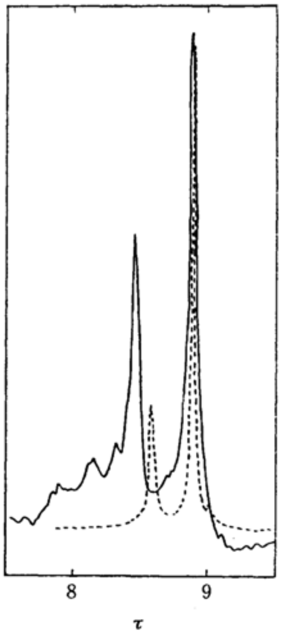

Fig. 1. NMR spectrum of alternate copolymer of acrylonitrile with isobutylene (——) and that of polyisobutylene (------).

The NMR spectrum shown in Fig. 1 was obtained in deuterated chloroform at 25°C by using TMS as a standard. The peak at 8.60 τ of methylene protons of polyisobutylene disappears completely, showing no existence of an isobutylene-isobutylene repeating unit, and a new peak appears at 8.40 τ in the spectrum of the copolymer. The strong peak at 8.85 τ corresponds to the strong peak at 8.89 τ of homopolymer of isobutylene which is ascribed

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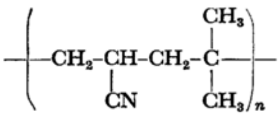
[1] G. E. Serniuk and R. T. Thomas, U. S. Pat. 3183217 (1965).

[2] N. G. Gaylord and A. Takahashi, paper presented at ACS Meeting, San Francisco, April 1968.

[3] M. Hirooka, H. Yabuuchi, S. Morita, S. Kawasumi and K. Nakaguchi, *J. Polymer Sci.*, *B*, **5**, 47 (1967).

to methyl protons, because the ratio of peak area at 8.40 τ of methylene protons to that at 8.85 τ of methyl protons in the copolymer is 4 : 6, whereas the area ratio of the peak at 8.60 τ to that at 8.89 τ in homopolyisobutylene is 2 : 6. Accordingly the copolymer may be a 1:1 copolymer of acrylonitrile and isobutylene and the 8.40 τ peak may be ascribed protons of the alternate copolymer. The following is the structure of the alternate copolymer.



$$-\left(-CH_2-\underset{CN}{CH}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-\right)_n-$$

We wish to express our thanks to Nippon Electric Varian, Ltd. for their cooperation in obtaining NMR spectra.