CHEMISTRY LETTERS, pp. 479-480, 1989.

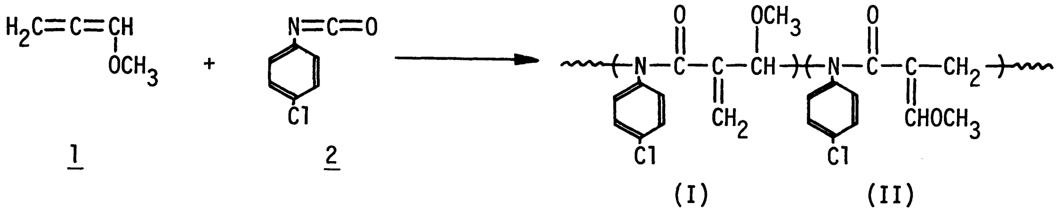
A Novel Spontaneous Alternating Copolymerization of Methoxyallene with 4-Chlorophenyl Isocyanate

Jiro MIZUYA, Tsutomu YOKOZAWA, and Takeshi ENDO*
Research Laboratory of Resources Utilization,
Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227

The spontaneous alternating copolymerization of methoxyallene with 4-chlorophenyl isocyanate proceeded through zwitterion to give polyamide having highly reactive exo-methylene groups bonded onto polymer backbone, accompanying the partial formation of β-lactam derivatives.

There has already been reported a number of spontaneous copolymerization of nucleophilic and electrophilic vinyl monomers.[1)] However, no work has been done on the spontaneous polymerization of allene derivatives which can be regarded as one of vinyl monomers bonded to another methylene carbon. In the course of our research on polymerization of allene derivatives, it has been recently found that the nucleophilic allene successfully reacted with the electrophilic allene to afford the alternating copolymer without an initiator.[2)] Furthermore, it is extremely interesting to estimate the copolymeriability of the nucleophilic allenes with the electrophilic heterocumulenes. Thus, we have found that the spontaneous copolymerization of methoxyallene (1) with various kinds of phenyl isocyanates takes place readily under mild conditions, and especially 1 reacted with 4-chlorophenyl isocyanate (2) to afford the alternating copolymer.

The reaction of 1 with 2 was carried out at 80 °C in acetonitrile without initiators to form the copolymer.[3)] The IR spectrum of the polymer obtained showed a characteristic carbonyl absorption at 1710 cm^{-1} based on a disubstituted amide.[4)] The ^{1}H NMR spectrum of the copolymer shows signals of olefinic protons at 6.2-5.5 and 5.3-4.8 ppm attributable to the vinyl ether and exo-methylene groups, respectively; these data support that allene 1 polymerizes by respective 1,2- and 2,3- double bonds, similarly to the radical polymerization.[5)] Furthermore, the absence of signals at 3.0-2.0 ppm due to $\gtrless C-CH_2-C\lessgtr$ group implied that the copolymer contained no homopolymer of 1.

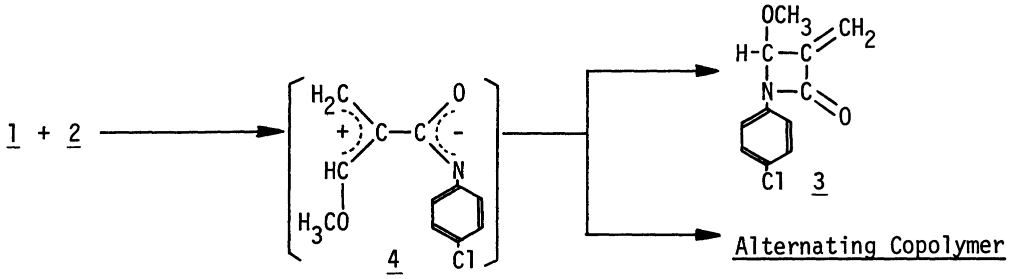


(1)

Further, from elemental analysis and ^{1}H NMR spectrum, the copolymer obtained was found to consist of 51% of 1 and 49% of 2,[6] and the ratio of unit (I) to (II) was 58:42 (Eq. 1).

In addition, 2-methylene-3-methoxy-N-(4-chlorophenyl)-β-propiolactam (3), which might be derived from the cyclization of zwitterion 4,[7] could be isolated from the hexane soluble part.[8] This strongly suggests that the 1:1 copolymer obtained here is the alternating structure formed by the successive reaction of zwitterion 4 (Eq. 2).

In summary, we can demonstrate a new spontaneous alternating copolymerization of an allene derivative with isocyanates through a zwitterionic mechanism. Thus, nucleophilic methoxyallene 1 successfully reacted with highly electrophilic 4-chlorophenyl isocyanate 2 to afford the alternating copolymer through zwitterion 4 which was ascertained by the isolation of cyclic compound 3.



References

1) H. K. Hall, Jr., Angew. Chem., Int. Ed. Engl., 22, 440 (1983).

2) J. Mizuya, T. Yokozawa, and T. Endo, J. Am. Chem. Soc., in press.

3) The sealed tube containing 1 (0.90 g, 10.0 mmol) and 2 (1.97 g, 10.0 mmol) was heated at 80 °C for 24 h in acetonitrile (5 M). The polymer was purified by dissolution in ether, followed by precipitation in hexane to give white polymer 0.17 g (24%); It was not a mixture of the homopolymers because both ones were insoluble in ether. $\overline{Mn}$=1300, $\overline{Mw}/\overline{Mn}$=1.30 (GPC based on PSt) ; Anal Found; H, 3.92%; C, 58.80%; N, 6.94%.

4) V. E. Shashoua, W. Sweeny, and R. F. Tietz, J. Am. Chem. Soc., 82, 866 (1960).

5) T. Yokozawa, M. Tanaka, and T. Endo, Chem. Lett., 1987, 1831.

6) The bulk copolymerization of 1 and 2 was carried out at 80 °C. The copolymer obtained consisted of 54% of 1 and 46% of 2.($\overline{Mn}$=870, $\overline{Mw}/\overline{Mn}$=3.46) And, in DMF, a reaction of 1 and 2 gave a cyclotrimer of 2 quantitatively.

7) Simple cyclization of zwitterion generated from allene derivatives and isocyanates was reported: E. J. Moriconi, and J. Kelly, J. Org. Chem., 33, 3036 (1968).

8) Propiolactam derivative 3 (0.16 g ;12%) was separated by the column chromatography using silica gel with ethyl acetate-hexane mixture from the soluble part (1.33 g): ^{1}H NMR(σ/$CDCl_3$) 7.70-7.10 (m, 4H), 5.95-5.75 (m, 2H), 5.45-5.35 (m, 1H), 3.25 (s, 3H) ppm; ^{13}C NMR(σ/$CDCl_3$) 159.8, 145.3, 136.0, 130.0, 129.4,118.0, 113.7, 86.6, 49.7 ppm; IR(neat) 1760 cm^{-1}; MS(m/e) 223 (M^+).

(Received November 30, 1988)