

Stereoregular Block Copolymers Obtained by a Radical Process in Inclusion Compounds¹

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Summary The 'living' character of the radical inclusion polymerization in pre-irradiated perhydrotriphenylene has been demonstrated by preparation of stereoregular block copolymers from diene monomers.

THE current interest in terminationless radical polymerizations² has prompted us to publish our results concerned with block copolymers obtained by radical polymerization in the solid state.

In previous papers³ we described a method of inclusion polymerization in perhydrotriphenylene (PHTP) based on the irradiation of the pure host and on the subsequent formation of an inclusion compound with suitable monomers. We showed there were two important features of this polymerization: (i) it exclusively occurs in the range of the thermodynamic stability of the inclusion compound PHTP-monomer, and (ii) the molecular weight of the polymer (all other conditions being the same) increases linearly with the polymerization yield. This latter fact suggests the absence, to a large extent, of termination and chain-transfer phenomena. Therefore, inclusion polymerization carried out under such conditions may be considered as a 'living' polymerization.

Proof of the 'living' nature of such a polymerization has been obtained by the synthesis of block copolymers. The process of their preparation is schematized as follows: (i) Irradiation of the pure host (PHTP) and formation of stable radicals entrapped in the crystalline matrix by using a ⁶⁰Co source. (ii) Formation of the inclusion compound with monomer (A) and its partial polymerization. (iii) Elimination of monomer (A): at this point, the solid phase consists of the inclusion compound PHTP-polymeric growing chains (A)_n* with active terminal radicals, and of non-complexed PHTP. (iv) Formation of the inclusion compound PHTP-monomer (B) and its final polymerization by the polymeric radicals.

All operations were carried out by high-vacuum techniques. Polymerizations were performed at room temperature and at a pressure ranging from the vapour pressure of the inclusion compound to that of the monomer. The general procedure has already been described.³

Butadiene, pentadiene, and isoprene, in different order and in different ratios, were used as the monomers (A) and (B). In all cases formation of block copolymers took place. I.r. and n.m.r. spectra of polymers (after elimination of PHTP) reveal the presence of both monomer units. In the

case of butadiene and pentadiene, the sequences of monomer units of the same type are quite long and highly regular. They exhibit a *trans*-1,4 structure in the case of butadiene and an isotactic *trans*-1,4 structure in the case of pentadiene. Sequence stereoregularity has been proved also by *X*-ray studies and differential thermal analysis (d.t.a.). Both methods show the presence of polybutadiene and polypentadiene crystalline blocks. D.t.a. curves of butadiene-containing copolymers show the characteristic first-order solid–solid transition of *trans*-1,4 polybutadiene in the range 50–70 °C.⁴

The butadiene–pentadiene copolymer is partially extracted by boiling hexane and both the soluble and the insoluble fractions contain long stereoregular sequences of the two

monomer units. This behaviour contrasts with that of the respective homopolymers with comparable molecular weight obtained in the same way.

Thus, definitive proof is obtained that inclusion polymerization in PHTP accomplished by pre-irradiation is a 'living' radical polymerization taking place inside a crystalline phase. The stability of the polymeric radicals which, after elimination of the first monomer, are situated on the boundary surface between two immiscible crystalline phases, is noteworthy.

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² V. A. Kabanov, *J. Polymer Sci.*, part C, *Polymer Symposia*, 1975, **50**, 71; V. Zubov, Communication presented at the 2nd U.S.S.R.–Japan Polymer Symposium, Kyoto, February 1976; A. Arfaei, R. N. Hazeldine, and S. Smith, *J.C.S. Chem. Comm.*, 1976, 260.

³ M. Farina, U. Pedretti, M. T. Gramagna, and G. Audisio, *Macromolecules*, 1970, **3**, 475; M. Farina, G. Audisio, and M. T. Gramagna, *ibid.*, 1971, **4**, 265; 1972, **5**, 617; M. Farina in 'Proceedings of the International Symposium on Macromolecules,' Rio de Janeiro, 1974, ed. E. B. Mano, Elsevier, Amsterdam, 1975, p. 21.

⁴ G. Natta, P. Corradini, and L. Porri, *Rend. Accad. Lincei*, 1956, **20**, 728; F. Danusso, *Polymer*, 1967, **8**, 281.