Polymer Bulletin 3, 339–346 (1980)

Polymer Bulletin

New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator-Transfer Agents (Inifers)

8. The Effects of Polymerization Conditions on the Functionality of Telechelic Polyisobutylenes

Victor S. C. Chang, Joseph P. Kennedy and Béla Ivan*

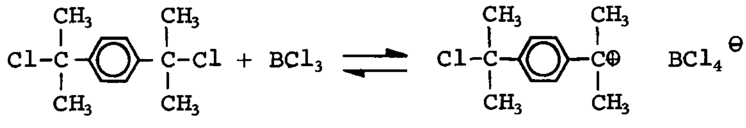
Institute of Polymer Science, The University of Akron, Akron, Ohio 44325, USA

Summary

The possibility of undesirable intramolecular cycloalkylation exists in the polymerization of isobutylene induced by the p-dicumyl chloride/BCl_3 inifer system. A scheme has been proposed which shows the sequence of reactions leading to indane skeletons. The structure of the indane derivatives has been characterized by ^1H NMR spectroscopy. Systematic experiments have been carried out using low isobutylene and high p-dicumyl chloride concentrations leading to polyisobutylene oligomers needed for accurate endgroup analysis. The effect of temperature, solvent composition (polar/nonpolar), isobutylene and BCl_3 concentration on the extent of indane skeleton formation has been investigated. Indane skeleton formation can be completely suppressed by the use of relatively nonpolar media, e.g., 1:1 mixture of CH_2Cl_2 :$\underline{n}$-C_6H_{14} , at or below -40°C, and conditions under which symmetrical telechelic polyisobutylenes can be obtained have been defined.

Introduction

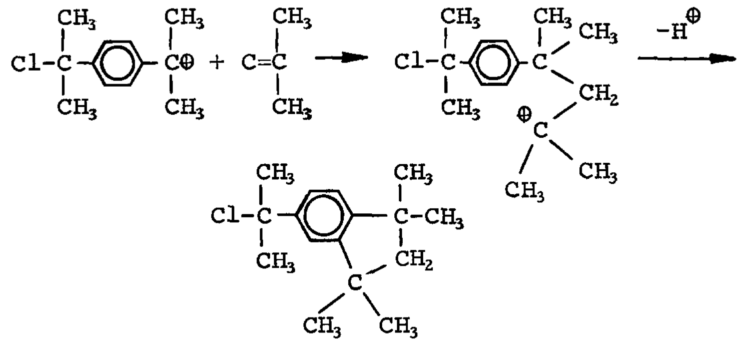
The synthesis by the inifer technique of a new telechelic polyisobutylene carrying two tertiary chlorine termini, Cl-PIB-Cl, has recently been accomplished (KENNEDY, SMITH 1980). Mechanism studies have revealed the existence of an undesirable side reaction, intramolecular cyclization, giving rise to a five-membered condensed ring system (indane skeleton) at the start of the polymer chain (CHANG 1980):



---

* Visiting Scientist; permanent address: Central Research Institute for Chemistry of the Hungarian Academy of Sciences, P.O.Box 17, 1525 Budapest, Hungary

0170-0839/80/0003/0339/$01.60



According to model experiments (CHANG, KENNEDY 1980) a second indane ring may also form. These side-reactions are unacceptable in the synthesis of terminally symmetrical bifunctional polyisobutylenes (IVAN, KENNEDY 1980).

This paper concerns an exploration of the mechanism of indane-skeleton formation during isobutylene polymerization by the p-dicumyl chloride/BCl_3 inifer system, in particular the definition of experimental conditions under which this side reaction could be avoided. In particular, the effects of temperature and solvent polarity on intramolecular cyclization have been investigated using very low monomer concentrations to insure the formation of low molecular weight polyisobutylenes suitable for endgroup analysis by ^1H NMR spectroscopy.

Experimental

The source and purification of materials has been described (KENNEDY, SMITH 1980). The p-dicumyl chloride, pDCC, was thoroughly purified by several recrystallizations from n-hexane; M_p 71^0. Polymerizations were carried out in culture tubes in a stainless steel enclosure under dry nitrogen and were terminated by adding prechilled methanol. The products were washed with dilute aqueous HCl, and distilled water, dried with anhydrous $MgSO_4$ and recovered by removing the solvent. ^1H NMR spectra were obtained on a Varian T-60 instrument, using 5-10% solutions in CCl_4.

The relative amounts of aromatic structures I, II, and III in Table I have been determined by integrating the 6.5 - 7.3 ppm region and calculating the relative areas of resonances centered at 6.62, 6.95 and 7.20 ppm by taking into consideration that these resonances, respectively, represent 2, 3 and 4 aromatic protons per molecule (CHANG, KENNEDY 1980).

Results and Discussion

^1H NMR analysis of several liquid telechelic Cl-PIB-Cl samples (M_n = 3500-4500) showed the existence of a small broad resonance centered at 6.95 ppm, close to the sharp singlet at 7.15 ppm associated with the four aromatic protons of the inifer fragment (see Figure 1).

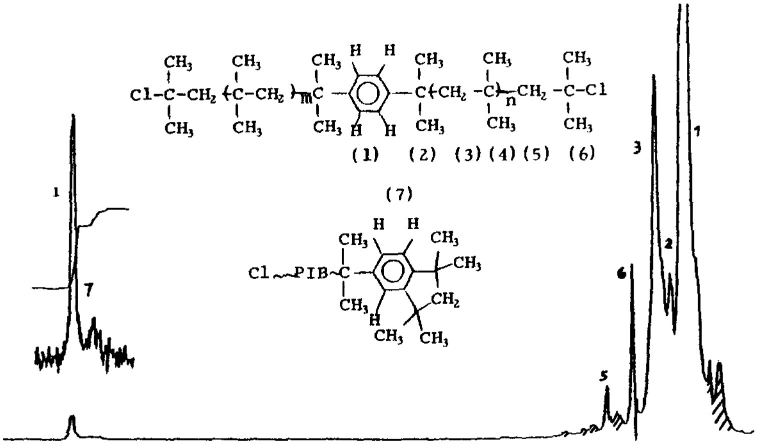
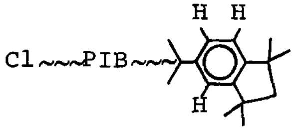


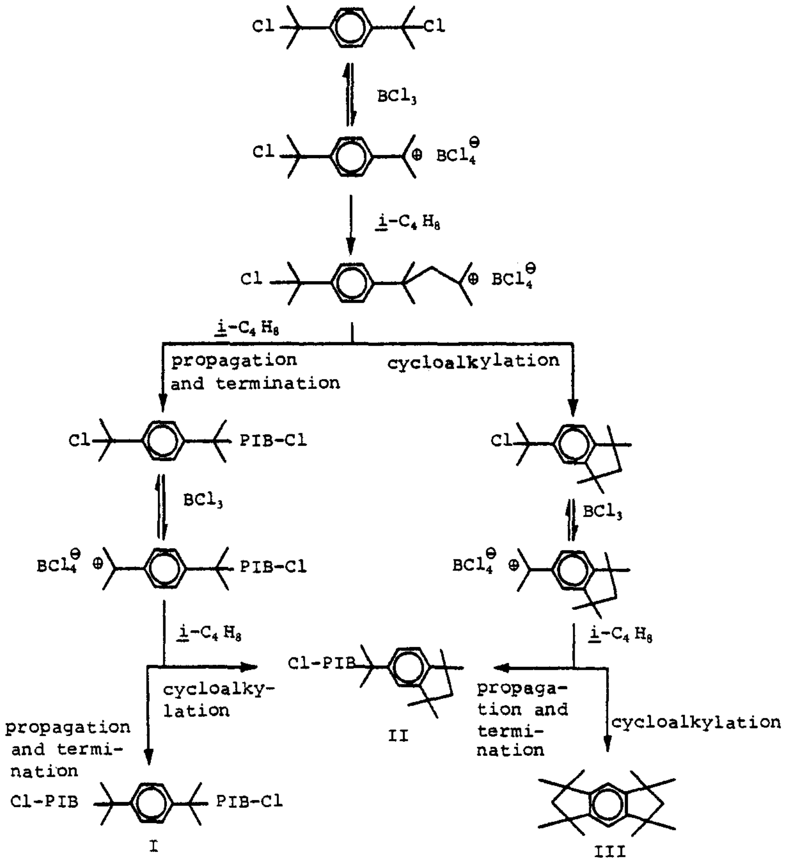
Figure 1. ^1H NMR Spectrum of Cl-PIB-Cl Obtained by the pDCC/BCl_3 Inifer System in CH_3Cl, [pDCC] = 2.0×10^{-2}M, [i-C_4H_8] = 0.5M, [BCl_3] = 6.0×10^{-2}M, Temperature = -50°

Comparison of this spectrum with those of two new model compounds, p-bis(3-chloro-1,1,3-trimethylbutyl) benzene and 1,1,3,3,5,5,7,7-octamethyl-s-hydrindacene, which show aromatic proton resonances at 7.20 and 6.62 ppm respectively and whose first synthesis and characterization has been described separately (CHANG, KENNEDY 1980) led to the assignment of the small resonance at 6.95 ppm to the aromatic proton resonances of an indane endgroup:



Scheme I shows the sequence of reactions leading to indane-skeletons by intramolecular cycloalkylation. Inspection of atomic models suggests that ring-closure would encounter little steric interdiction. The mechanism of cycloalkylation during the first addition step of this pDCC-induced isobutylene polymerization and that occurring during chain transfer to monomer in cationic α-methylstyrene polymerization (DAINTON, Scheme I

Polymerization of Isobutylene Induced by the pDCC/BCl_3 Inifer System



TOMLINSON 1953; LENZ et al. 1973) are fundamentally similar. Related intramolecular cycloalkylations have also been proposed in a variety of other systems (BERTOLI, PLESCH 1968; HIGASHIMURA et al. 1979; WOLOVSKY, MAOZ 1973).

The Effect of Reaction Conditions on Indane Formation

To gain reliable information how to avoid cycloalkylation during isobutylene polymerization by the pDCC/BCl_3 inifer system, a series of polymerizations have been carried out in the presence of relatively low monomer and high pDCC concentrations. Under these conditions relatively low molecular weight products ($M_n < 450$) facilitating endgroup analysis by ^1H NMR spectroscopy are obtained. Table I shows the conditions employed and the relative amounts of the three aromatic structures I, II, and III in Scheme 1 calculated from the raw data shown in Figure 2.

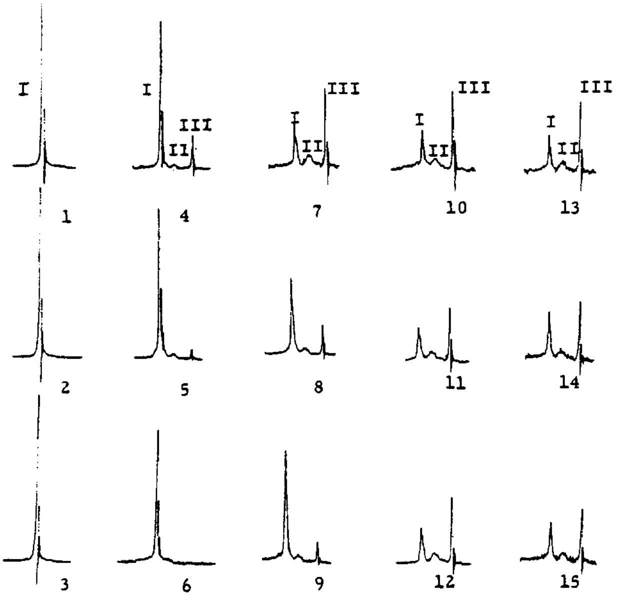


Figure 2. Aromatic Proton Resonances of Products I, II and III shown in Scheme I. Respective Resonances: I δ = 7.15 ppm; II 6.95 ppm; III 6.62 ppm

Among the four parameters studied the effect of temperature and solvent composition are decisive for cycloalkylation: decreasing the temperature and/or the polarity of the medium increases the relative

Table I

Model Experiments of Indane Formation[a]

No.	Temp. °C	Solvent Composition %		i-C_4H_8	BCl_3	Products[b] %		
		CH_2Cl_2	n-hexane	molex10^3	molex10^3	I	II	III
1	-40	50	50	2.6	3.25	100.0	0.0	0.0
2	-60	50	50	2.6	3.25	100.0	0.0	0.0
3	-80	50	50	2.6	3.25	100.0	0.0	0.0
4	-40	75	25	2.6	3.25	63.3	12.5	24.2
5	-60	75	25	2.6	3.25	81.1	9.0	9.9
6	-80	75	25	2.6	3.25	97.0	3.0	0.0
7	-40	100	0	2.6	3.25	25.7	22.9	51.4
8	-60	100	0	2.6	3.25	57.7	22.2	20.1
9	-80	100	0	2.6	3.25	75.5	14.0	10.5
10	-40	100	0	1.3[c]	3.25	24.1	24.1	51.8
11	-40	100	0	3.9[c]	3.25	26.3	22.8	50.8
12	-40	100	0	5.2[c]	3.25	27.2	24.3	48.5
13	-40	100	0	2.6	0.65	23.5	23.0	53.5
14	-40	100	0	2.6	1.30	30.9	22.5	46.6
15	-40	100	0	2.6	5.20	31.5	22.0	46.5

a. [pDCC] = 6.5×10^{-4} mole, total volume = 50 ml

b. Estimated by integrating ^1H NMR spectra shown in Figure 2. Accuracy ± 5 mole %

c. Slight change in volume not compensated amount of the desirable product and suppresses indane-skeleton formation. Indeed, cycloalkylation can be avoided at or below -40^0 by the use of a relatively weakly polar (1:1 CH_2Cl_2:n-C_6H_{14}) medium (Expts. 1-3). In contrast, cycloalkylation cannot be completely frozen out in pure CH_2Cl_2 even at -80^{0}C. In a medium of intermediate polarity (3:1 CH_2Cl_2:n-C_6H_{14}) indane formation can be largely but not completely eliminated by cooling to -80^{0}C (Expts. 4-6). The combined effects of temperature and solvent composition on I content is shown in Figure 3. Compared to these effects, the influence of [i-C_4H_8] and [BCl_3] on indane content are modest (Expts. 10-12 and 13-15, respectively).

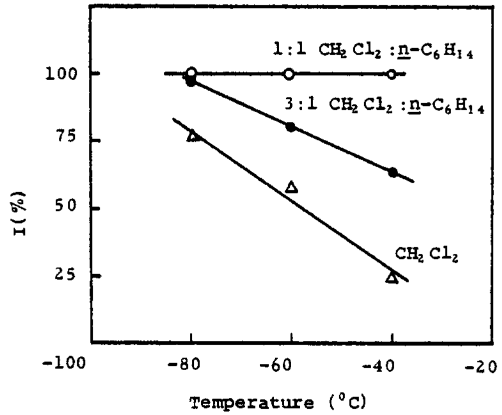


Figure 3. The Effect of Temperature on the Relative Amount of Structure I at Various Solvent Compositions

The main purpose of this research was to define conditions under which perfectly bifunctional ($\overline{F}_n$ = 2.0) telechelic PIB's can be obtained and cycloalkylation can be avoided in the pDCC/BCl_3/i-C_4H_8 system. In the presence of low [i-C_4H_8] and high [pDCC] the rate of cycloalkylation is favored; the fact that we were able to suppress this reaction under these "model" conditions, gives us great confidence that indane-skeleton formation can be readily avoided in the presence of high [i-C_4H_8] and low [pDCC], i.e., under true polymerization conditions. These expectations have indeed been routinely corroborated in our continuing investigations.

Acknowledgement

Financial support by the NSF (Grant INT-78-27245), the Institute for Cultural Relations, Hungary, and the Firestone Tire and Rubber Company is gratefully acknowledged.

References

BERTOLI, V. and PLESCH, P. H.: J. Chem. Soc. (B), 1500 (1968)

CHANG, V. S. C.: Ph.D. Dissertation, The University of Akron, 1980

CHANG, V. S. C. and KENNEDY, J. P.: to be published

DAINTON, F. S. and TOMLINSON, R. H.: J. Chem. Soc., 151 (1953)

HIGASHIMURA, T., HIZA, M. and HASEGAWA, H.: Macromol., 12, 1058 (1979)

IVAN, B. and KENNEDY, J. P.: Polymer Bulletin, 2, 351 (1980)

KENNEDY, J. P. and SMITH, R. A.: J. Polym. Sci., Polym. Chem. Ed., 18, 1523 (1980)

LENZ, R. W., SUTHERLAND, J. E. and WESTFELT, L. C.: 3rd International Cationic Symposium, C22, Rouen, France, 1973

WOLOVSKY, R. and MAOZ, N.: J. Org. Chem., 38, 4040 (1973)

Received October 16, 198o