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IDENTIFICATION OF INITIATOR FRAGMENTS IN POLYISOBUTYLENE BY NMR SPECTROSCOPY

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ABSTRACT

Deuterated polyisobutylenes carrying protonated initiator fragments were prepared by the living polymerization technique employing perdeuterated isobutylene [$\text{CD}_2=\text{C}(\text{CD}_3)_2$] and select protonated initiators (see Scheme 1). The polymers were analyzed by ¹H- and ¹³C-NMR spectroscopy, and the resonances due to the protic initiator fragments were unequivocally assigned. The assignments of ¹³C-NMR signals were affected by the distortionless enhancement by polarization transfer mode of spectra accumulation.

INTRODUCTION

The structure of polymers accurately reflects the polymerization mechanism, and NMR spectroscopy has extensively been used to generate the needed structural information. Thus, for example, polyisobutylenes (PIBs) prepared by the inifer

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splitting due to the spin-spin interaction with deuterium ($I = 1$), and altered response to DEPT pulse sequence]. For example, the resonance for CDH_2 appears as a triplet at a higher field (relative to CH_3) with the same phasing as CH_2 . In this manner, unambiguous assignments can readily be made.

This method was successfully employed in the endgroup analysis of polydienes obtained with organolithium initiators [11, 12] and rare-earth catalysts [13]. A similar approach was also used for the analysis of styrene-butadiene [14] and styrene-maleic anhydride [15] copolymers. A complimentary method utilizes the transfer of polarization from deuterium to carbon, leaving in the spectra only signals of carbons connected to deuterium [16, 17]. This method was applied to gain insight into the mechanism of metathesis polymerization of norbornene [18] and transesterification of styrene-methyl methacrylate copolymer [19].

EXPERIMENTAL

NMR Spectroscopy

NMR spectra were obtained by a Varian Gemini-200 spectrometer operating at 200 and 50 MHz for ^1H and ^{13}C , respectively, using 5 mm tubes and CDCl_3 solutions at ambient temperature. Sample concentrations were 20 mg/mL for proton and 250 mg/mL for carbon spectroscopy. TMS was used as the internal standard. Typically, 128 transients were accumulated for the proton spectra with 60° pulses (18 μs), 2.7 seconds acquisition time, and 2 seconds delay. ^{13}C -NMR spectra were obtained with the ^1H decoupler "on" only during the acquisition time to suppress the NOE. The following parameters were used: 60° pulses (14.7 μs), 1024 transients, 1 second acquisition time, and 2 seconds delay. Under these conditions quantitative ^1H and ^{13}C spectra were obtained since T_1 for both nuclei was less than 1 second (except for quaternary carbons) [20]. DEPT [10] spectra were obtained using a standard Gemini microprogram and the following conditions: 1024 transients, 1 second acquisition time, 2 seconds delay, the widths of the 90° pulses were 27 μs for protons and 22 μs for carbons. $^1J(\text{C},\text{H})$ was set to 130 Hz, and the multiplicity parameters were 0.5 (this corresponds to $\Theta = 45^\circ$ in the original publication [10]) and 1.5 ($\Theta = 135^\circ$). The corresponding spectra are denoted DEPT- 45° and DEPT- 135° .

Polymerization

Living isobutylene polymerizations were induced by the following three initiators: 2-chloro-2,4,4-trimethylpentane (TMPCl) [7], 1,4-bis(1-hydroxy-1-methylethyl)benzene (DiCumOH) [21], and 1,3-bis(1-hydroxy-1-methylethyl)-5-*tert*-butylbenzene (*t*-BuDiCumOH) [5, 21] in conjunction with BCl_3 coinitiator and *N,N*-dimethylacetamide (DMA) electron donor in CH_2Cl_2 diluent at -80°C . Further experimental details, including concentrations, are shown in Table 1.

Monomer Synthesis

Perdeuterated isobutylene was obtained according to Ref. 22 by the dehydration of *tert*-butanol- d_{10} (isotope ^2H content $\sim 80\%$). Thus a mixture of 9.9 g $\text{C}_4\text{D}_9\text{OD}$ and 10 g oxalic acid was heated at $95\text{--}97^\circ\text{C}$ for 3 hours, the gaseous $\text{CD}_2\text{C}(\text{CD}_3)_2$ was passed through aqueous KOH and anhydrous CaCl_2 , and con-

TABLE 1. Synthesis of Polyisobutylenes via Living Carbocationic Polymerization^a

Run	Initiator	Monomer	Yield, g (%)	\bar{M}_n , g/mol	\bar{M}_w/\bar{M}_n
1H	TMPCI	C ₄ H ₈	0.77 (93)	1200	1.14
1D	TMPCI	C ₄ D ₈	0.82 (90)	1150	1.15
2H	DiCumOH	C ₄ H ₈	0.76 (85)	1250	1.15
2D	DiCumOH	C ₄ D ₈	0.82 (85)	1200	1.20
3H	<i>t</i> -BuDiCumOH	C ₄ H ₈	0.78 (84)	1300	1.13
3D	<i>t</i> -BuDiCumOH	C ₄ D ₈	0.87 (86)	1300	1.16

^a[Initiator]₀ = 72 mmol/L; [IB]₀ = 1.28 mol/L; [BCl₃] = 0.72 mol/L; [DMA] = 72 mmol/L; methyl chloride; -80°C; 3 hours; V = 10 mL.

densed in an ampule cooled by dry ice/ethanol. Yield = 6.4 g (85%). The liquid *i*C₄D₈ was stored in a sealed ampule over CaH₂ at room temperature for 1 week and was recondensed before use.

RESULTS AND DISCUSSION

¹³C-NMR Spectroscopy

Scheme 1 shows the initiators used, outlines the living polymerizations undertaken, and the polymer structures obtained. The \bar{M}_n and molecular weight distributions (\bar{M}_w/\bar{M}_n) together with experimental details are collected in Table 1.

Figure 1 shows the ¹³C-NMR spectra of polymers **1H** and **1D** and the DEPT-135° spectrum of the latter. A dramatic simplification of the ¹³C-NMR spectrum obtained with the polymer prepared with the perdeuterated isobutylene and using the DEPT accumulation mode, relative to that of the conventional ¹³C spectrum, is clearly evident. In DEPT-135° spectra the carbons bonded to an odd number of hydrogens (i.e., CH, CHD, CHD₂, and CH₃) produce signals with positive amplitudes while carbons connected to an even number of hydrogens (i.e., CH₂ and CH₂D) give signals with negative amplitudes. The DEPT-135° spectrum of polymer **1D** (Fig. 1c) shows two sharp positive signals at 30.7 and 32.4 ppm, and one negative signal at 58.2 ppm. The two positive signals are due to two types of methyl groups, whereas the negative signal is due to the methylene group of the initiator (TMPCI) fragment in the PIB. The two methyl signals are easily assigned according to their integral intensities in the quantitative spectrum 1a. Thus the signal at 32.4 ppm is due to the methyls in the *t*-Bu headgroup, whereas that at 30.7 ppm corresponds to the methyls next to it: *t*-Bu-CH₂-C(CH₃)₂-PIB. These assignments are in agreement with those proposed in Ref. 8 on the basis of the additivity scheme of Grant and Paul [23] (a slight deviation in the values is probably due to differences in spectra referencing and/or sample concentrations). However, the negative signal due to the methylene group of the TMPCI initiator fragment should be reassigned: It appears at the highest field among other methylene signals (58.2 ppm). All assignments are summarized in Fig. 2.

The small unresolved signals at ~59 and ~30 ppm in spectrum 1c are due to carbons bonded to residual protons of incompletely deuterated isobutylene units

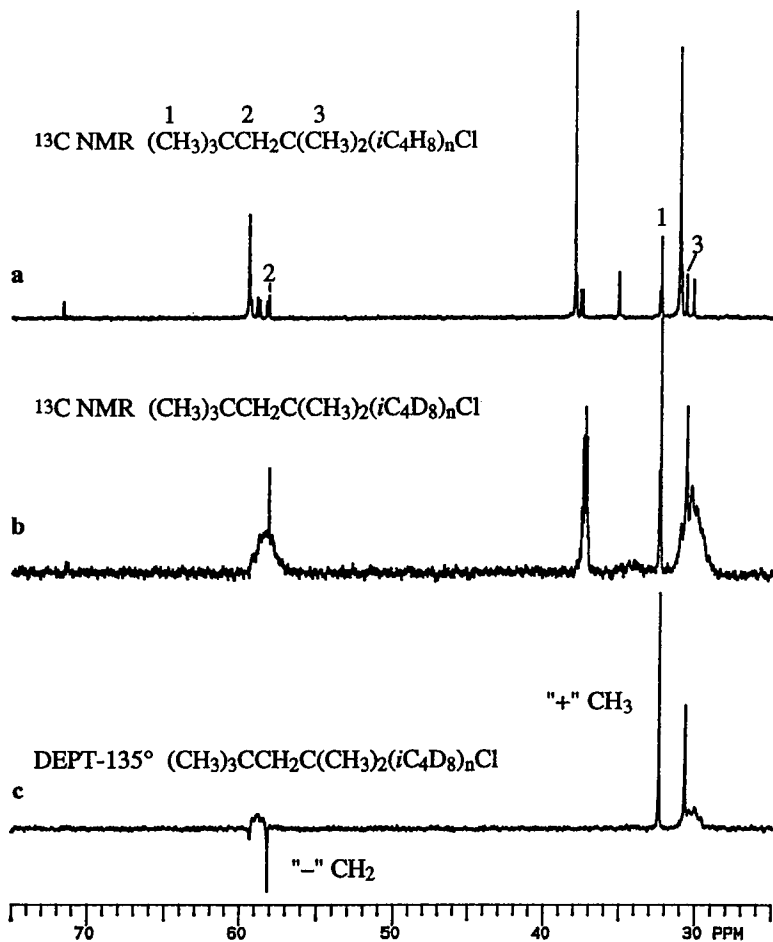


FIG. 1. (a) ^{13}C -NMR (50 MHz) spectrum of polymer 1H. (b) ^{13}C -NMR spectrum of polymer 1D. (c) DEPT- 135° spectrum of polymer 1D. See Scheme 1.

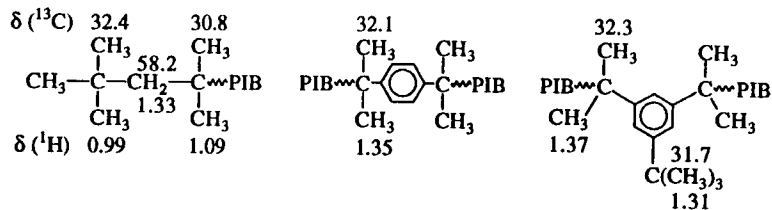


FIG. 2. ^{13}C and ^1H chemical shifts and assignments of initiator fragments in polyisobutylenes.

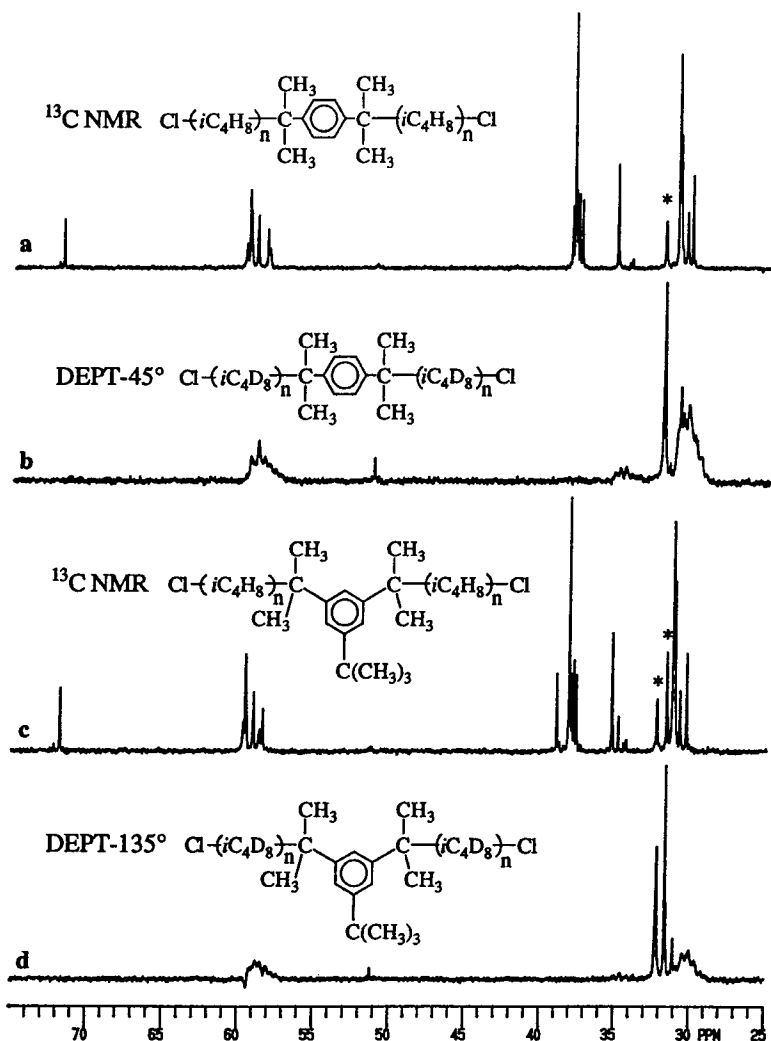


FIG. 3. (a) ^{13}C -NMR spectrum of polymer 2H. (b) DEPT-45° spectrum of polymer 2D. (c) ^{13}C -NMR spectrum of polymer 3H. (d) DEPT-135° spectrum of polymer 3D. See Scheme 1.

(degree of deuteration $\sim 80\%$). These signals are shifted upfield relative to the corresponding signals shown in spectrum 1a and are split by spin-spin interaction with deuterium.

To estimate a possible long range isotopic shift induced by deuterated isobutylene units, the DEPT-45° spectrum of a mixture of protonated and deuterated polymers 1H and 1D was also recorded (not shown). A small but discernible split of 0.06 ppm was observed only for the 30.8 ppm signal of methyls next to the *tert*-butyl headgroup.

Figure 3 shows the spectra of polymers obtained with DiCumOH and *t*-BuDiCumOH initiators. Only the aliphatic regions are shown, since the assign-

ments of the aromatic signals are straightforward. The signals due to the initiator fragments are marked by asterisks, and the chemical shifts are listed in Fig. 2.

The spectrum of the mixture of polymers **2H** and **2D** revealed an upfield isotopic shift (0.07 ppm) for the signal at 32.1 ppm detected by its splitting. The same effect was observed in the spectrum of the mixture of polymers **3H** and **3D** for the signal at 32.3 ppm.

Spectra 3b and 3d demonstrate the advantage of the DEPT-135° spectrum relative to that of DEPT-45°. The latter is not selective and all protonated carbons (CH_n) give positive signals. Thus the signals of main chain carbons bonded to residual protons are stronger in spectrum 3b than in spectrum 3d. In contrast, in spectrum 3d (DEPT-135°) the positive signals due to CHD , CHD_2 , and CH_3 are

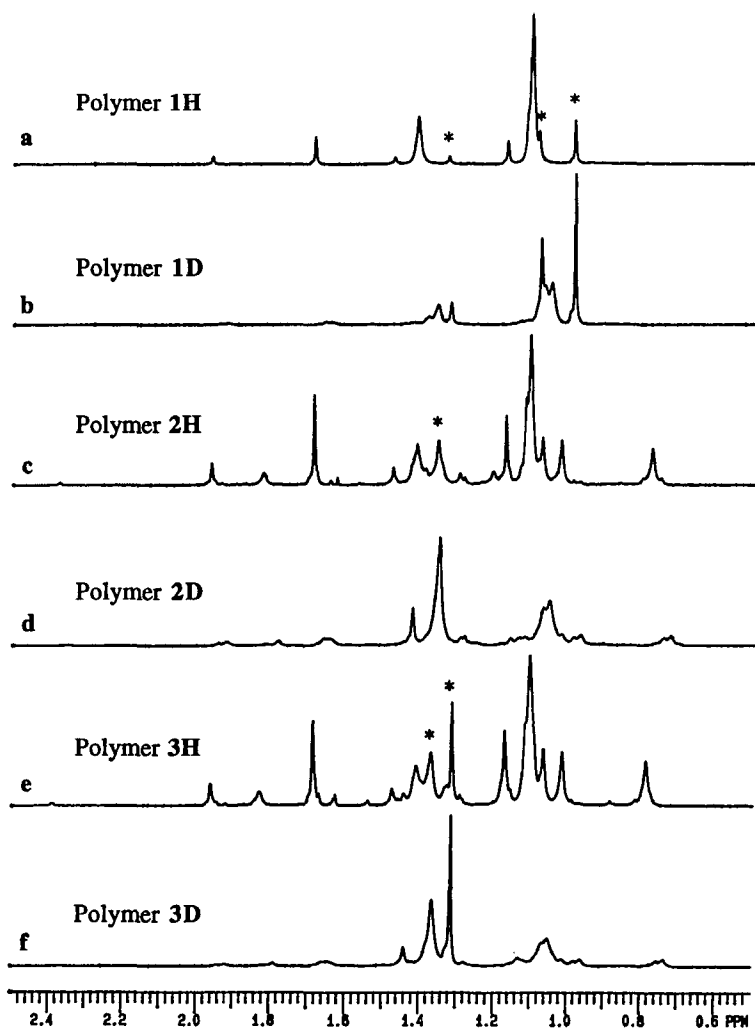


FIG. 4. ¹H-NMR (200 MHz) spectra of polymers: (a) **1H**; (b) **1D**; (c) **2H**; (d) **2D**; (e) **3H**; (f) **3D**. See Scheme 1.

partially offset by the negative signals due to the CH₂ and CH₂D groups which reduce the overall intensity of the resonances.

¹H-NMR Spectroscopy

The same six polymers (Scheme 1) were also used to assign ¹H resonances. Because of the use of deuterated monomer in the polymerization, the signals due to the repeat units are reduced in proportion to the degree of deuteration. Consequently the signals of the initiator fragments become more pronounced, and unequivocal fragment assignment becomes possible. Figure 4 shows the spectra of PIBs **1H-3D** (see Scheme 1 and Table 1). The signals of the TMPCl fragment (spectra 4a and 4b) were assigned according to their integral intensities, while those of the *t*-BuDiCumOH fragment were assigned by comparing spectra 4d and 4f. In the latter an additional signal appears at 1.31 ppm due to the *tert*-butyl group of *t*-BuDiCumOH initiator fragment. All assignments are collected in Fig. 2.

Spectra of mixtures of polymers **1H** and **1D**, **2H** and **2D**, and **3H** and **3D** showed that only the signals at 1.09 and 1.33 ppm of the TMPCl initiator fragment exhibit the upfield isotopic shift noticeable by splitting. The magnitude of this shift for both signals was 0.007 ppm.

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REFERENCES AND NOTES

- [1] J. P. Kennedy and R. A. Smith, *Polym. Prepr.*, **20**(2), 316 (1979).
- [2] R. Faust and J. P. Kennedy, *Polym. Bull.*, **15**, 317 (1986).
- [3] M. Tessier, N. A. Hung, and E. Maréchal, *Ibid.*, **4**, 111 (1981).
- [4] M. Tessier and E. Maréchal, *Ibid.*, **10**, 152 (1983).
- [5] R. Santos, J. P. Kennedy, and M. Walters, *Ibid.*, **11**, 261 (1984).
- [6] M. K. Mishra, E. Santee, and J. P. Kennedy, *Ibid.*, **15**, 469 (1986).
- [7] G. Kaszas, J. E. Puskas, C. C. Chen, and J. P. Kennedy, *Ibid.*, **20**, 413 (1988).
- [8] S. Nemes, J. Si, and J. P. Kennedy, *Ibid.*, **23**, 597 (1990).
- [9] J. Si and J. P. Kennedy, *J. Polym. Sci., Polym. Chem.*, In Press.
- [10] D. M. Doddrell, D. T. Pegg, and M. R. Bendall, *J. Magn. Reson.*, **48**, 323 (1982).
- [11] A. V. Lubnin, L. V. Osetrova, and I. S. Podkorytov, *Zh. Obshchei Khim. (USSR)*, **59**, 1159 (1989); *J. Gen. Chem. (English translation)*, **59**, 1024 (1989).
- [12] I. S. Podkorytov and A. V. Lubnin, *Magn. Reson. Chem.*, **29**, 561 (1991).
- [13] K. D. Skuratov, M. I. Lobach, A. N. Shibaeva, L. A. Churlyayeva, T. V. Erokhina, L. V. Osetrova, and V. A. Kormer, *Polymer*, **33**, 5202 (1993).

- [14] H. Sato, T. Ishikawa, K. Takebayashi, and Y. Tanaka, *Macromolecules*, **22**, 1748 (1989).
- [15] G. B. Butler, C. H. Do, and M. C. Zerner, *J. Macromol. Sci. — Chem.*, **A26**, 1115 (1989).
- [16] P. L. Rinaldi and N. J. Baldwin, *J. Am. Chem. Soc.*, **104**, 5791 (1982).
- [17] P. L. Rinaldi and N. J. Baldwin, *Ibid.*, **105**, 7523 (1983).
- [18] J. A. Johnston, M. Tokles, G. S. Hatvany, P. L. Rinaldi, and M. F. Farona, *Macromolecules*, **24**, 5532 (1991).
- [19] P. L. Rinaldi, D. R. Hensley, M. Tokles, G. S. Hatvany, and H. J. Harwood, *Ibid.*, **25**, 7398 (1992).
- [20] The analysis of T_1 values will be reported elsewhere.
- [21] C. C. Chen, G. Kaszas, J. E. Puskas, and J. P. Kennedy, *Polym. Bull.*, **22**, 463 (1989).
- [22] D. H. Hey, R. J. Nicholls, and C. W. Pritchett, *J. Chem. Soc.*, p. 97 (1944).
- [23] D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, **86**, 2984 (1964).

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