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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Kennedy, Joseph P. and Nakao, M.(1977) 'Copolymerization of Isobutylene with α -Pinene', Journal of Macromolecular Science, Part A, 11: 9, 1621 – 1636

To link to this Article: DOI: 10.1080/00222337708063080

URL: <http://dx.doi.org/10.1080/00222337708063080>

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Copolymerization of Isobutylene with α -Pinene

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ABSTRACT

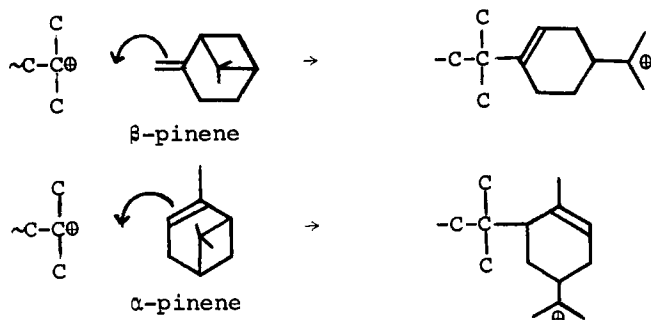
The copolymerization of isobutylene with α -pinene has been investigated by using EtAlCl_2 in ethyl chloride diluent at ca. -105°C . The copolymerizations proceeded readily and gave random copolymers of reasonably high molecular weights. Copolymer homogeneity, composition and structure was investigated by GPC, solubility behavior, PMR (60 and 300 MHz), CMR, reactivity ratio determination, and vulcanization behavior.

INTRODUCTION

Having completed our extended investigations concerning the copolymerization of isobutylene and β -pinene [1-3], we became interested in exploring the possibility of copolymerization of

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isobutylene with α -pinene. While cross-propagation with β -pinene was expected and indeed occurred with greatest ease [1], this reaction was thought to be much less favorable with the α -isomer because of its internal (endo) unsaturation.



The rate of addition of isobutylene to the growing ends formed from either pinene isomer is probably similar and was anticipated not to be rate determining.

The copolymerization of isobutylene with α - and β -pinenes has already been investigated by Finnish authors [4], who added BF_3 and AlCl_3 in CH_2Cl_2 to isobutylene/ α - or β -pinene charges in the -10 to -50° range, and solely on the basis of some GPC data concluded that these copolymerizations do not take place, rather mixtures of homopolymers are formed.

We have obtained poly(isobutylene-co- β -pinene) under conditions quite similar to those employed by the Finnish workers except working at low conversions and criticized their conclusions [1]. Our present research concerning the copolymerization of isobutylene with α -pinene leads us again to the conclusion that random copolymerization can be achieved under conditions not too dissimilar to those employed by the Finnish investigators, i.e., at lower conversions and with more suitable charge composition.

In addition to the work of Sivola and Harva [4], a patent claims the copolymerization of isobutylene with a variety of terpenes, and in particular with α -pinene [5]; however, none of the previous authors have investigated the mechanism of copolymerization and/or have characterized the products obtained.

This paper concerns the copolymerization of isobutylene with α -pinene with the use of EtAlCl_2 in ethyl chloride diluent at low temperatures (ca. -105°C). According to our results, isobutylene

and α -pinene can be copolymerized to reasonably high molecular weight random materials. The homogeneity and the random nature of the copolymers was examined by gel-permeation chromatography, solubility behavior, high resolution PMR spectroscopy, crosslinking experiments, and by the application of the Kelen-Tüdös copolymerization equation.

EXPERIMENTAL

Materials

α -Pinene (Aldrich Chemical Company, Inc.) was dried over calcium hydride and freshly distilled under reduced pressure before use. Gas chromatography of the purified material showed 98.5% purity and the presence of two major and two trace impurities, all higher boiling than α -pinene. $C_2H_5AlCl_2$ (Ethyl Corp.) was also vacuum-distilled twice in the dry box before use. Isobutylene (Union Carbide Co.) and ethyl chloride (Union Carbide Co.) were dried by passing these gases through glass columns packed with a mixture of porous barium oxide (Barium and Chemicals, Inc.) and Molecular Sieves (Linde Type 3A, Matheson, Coleman and Bell).

Polymerization

All polymerization and material transfers were carried out in a dry box under a nitrogen atmosphere (moisture level 10-30 ppm). Polymerizations were carried out in three-necked flasks equipped with mechanical stirrer and thermometer and immersed in a cooling bath. The charges [monomer(s) in ethyl chloride] were cooled, and prechilled $C_2H_5AlCl_2$ in ethyl chloride was added to initiate polymerizations. Reactions were fast and exothermic ($\sim 10^\circ C$). Polymerizations were terminated by the addition of methanol. The crude products were dissolved in cyclohexane in a separatory funnel, the coinitiator ($C_2H_5AlCl_2$) residues were removed by dissolving in an aqueous HCl solution and cyclohexane layer (250 ml) containing the polymers was precipitated into 1500 ml methanol. The methanol-insoluble fraction was filtered, dried, and weighed. The methanol-soluble low molecular weight fraction was also collected by evaporating the methanol and weighing.

Characterization

Intrinsic viscosities were measured by using diisobutylene solvent at 20°C and a Ubbelohde viscometer. While the relationship between molecular weight and intrinsic viscosity for each copolymer composition was not established, an approximate \overline{M}_v was obtained from Eq. (1) derived for polyisobutylene [6].

$$\ln \overline{M}_v = 12.48 + 1.565 \ln [\eta] \quad (1)$$

Number-average molecular weights were determined by osmometry by using a 503 High Speed Osmometer (Mechrolab Inc.), 08S8S membrane (ARRO Laboratories, Inc.) suitable for \overline{M}_n in the 10^4 - 10^6 range, and toluene solvent at 37.9°C. The π/c versus concentration plots gave straight lines in the concentration range from 0.5 to 10 g/liter. Number-average molecular weights of low molecular weight samples were determined by vapor pressure osmometry with a Hitachi Perkin-Elmer Coleman 115 (Hitachi, Ltd.) instrument and toluene solvent.

Gel-permeation chromatography was carried out at 25°C on an Ana-Prep chromatograph (Waters Associates) using four matched columns: 1.5×10^5 - 7×10^5 Å, 5×10^4 - 1.5×10^5 Å, 1.5×10^4 - 5×10^4 Å, 5×10^3 - 1.5×10^4 Å at 70 psi and 1 ml/min flow rate. The concentration of the samples was 0.25 g/100 ml in THF.

Solubility and phase separation studies were carried out with blends of homopolymers and with copolymer samples in cyclohexane solvent in graduated 20 ml cylinders at room temperature. The \overline{M}_n of polyisobutylenes used in these experiments was 2.9×10^4 by GPC. The preparation and characteristics of poly- α -pinenes are described in Table 1. The solvent was slowly evaporated by letting the uncovered cylinders stand at room temperature in the hood.

Copolymer composition was determined from PMR spectra obtained on a Varian T-60 nuclear magnetic resonance spectrometer in CCl_4 solutions and with TMS as internal reference. Equation (2) was derived to calculate the relative amounts of isobutylene and α -pinene in the copolymer

$$\alpha\% = 100B/(3A + B) \quad (2)$$

where $\alpha\%$ is mole percent α -pinene, A is the area associated with methylene protons of the isobutylene unit at 1.4 ppm, and B is the

area associated with methylene and methyne protons of the α -pinene unit at 1.8 ppm. Resolution of chemical shifts in the methyl region (0.8-1.1 ppm) was obtained by using a high-resolution (300 MHz) Varian Model HR 300 NMR spectrometer.

¹³C-NMR spectroscopy was carried out at 32°C by Varian CFT-20 NMR spectrometer using CDCl₃ solutions and hexamethyldisiloxane as internal reference.

The crosslinking of copolymer samples was carried out by the use of S₂Cl₂ at room temperature. The samples were dissolved in THF (5 wt % solutions), and 3 wt % S₂Cl₂ (on solid copolymer) was added. Since gel did not form after 24 hr, an additional 6 wt % S₂Cl₂ was added. After 5 days of shaking, gel formed. The gel was extracted by THF, dried, and weighed. The THF-soluble fraction was stored for 15 additional days. The subsequently formed gel was recovered by filtration, drying, and weighing. Polyisobutylene and poly- α -pinene controls showed no sign of gelation under the same conditions.

RESULTS AND DISCUSSION

Preliminary small-scale experimentation guided us to design suitable synthesis conditions to produce and collect sufficient material for characterization studies. Polymerizations proceeded smoothly to sufficiently low (10-20%) conversions required for meaningful copolymer analysis. Table 1 shows synthesis and characterization results. The latter were obtained from homogeneity (GPC, high resolution PMR, solubility, and crosslinking studies), composition (PMR) and molecular weight (membrane and vapor phase osmometry, and viscometry) determinations. An analysis of this information leads us to conclude that isobutylene and α -pinene can be copolymerized to reasonably high molecular weight materials and that α -pinene units are probably randomly distributed in the copolymer chain.

Gel-Permeation Chromatography

Product homogeneity has been investigated by gel-permeation chromatography. The GPC traces of the four samples described in Table 1 are shown in Fig. 1. All the traces were unimodal and virtually symmetrical, suggesting the presence of reasonably homogeneous materials. The traces shift toward higher elution count (lower molecular weights) with increasing α -pinene content, indicating the molecular weight-depressing effect of increasing

TABLE 1. Synthesis and Characterization of Poly(isobutylene-co- α -pinene)

Synthesis details	Expt. 20	Expt. 21	Expt. 22	Expt. 23
Volume of monomers used (ml) ^a				
Isobutylene	-	14.3	23.8	33.3
α -Pinene	95.3	66.7	47.6	28.6
α -Pinene monomer feed (mole %)	100	70	50	30
Volume of EtAlCl ₂ solution used (ml) ^b	16.5	8.2	4.1	2.1
Temperature range (°C)	-102 to -109	-90 to -107	-89 to -103	-100 to -107
Polymerization time (min)	60	30	10	10
Conversion (g/wt %)	6.882/8.4	7.753/11.5	9.903/17.1	9.520/19.8
MeOH-insoluble (g/wt %)	6.683/8.2	7.561/11.2	9.807/16.9	9.502/19.8
MeOH-soluble (g/wt %)	0.199/0.2	0.192/0.3	0.096/0.2	0.018/0.0
Characterization				
α -Pinene composition in copolymer (mole %)	100	9.9	8.2	3.2
$\bar{M}_n \times 10^{-4}$ by osmometry		1.2	1.5	2.9
by VPO	0.32	1.1	-	-
$[\eta]$ (20°C, diisobutylene)	0.046	0.116	0.180	0.310
$\bar{M}_v \times 10^{-4}$ c	-	0.9	1.8	4.2

Physical appearance	Brittle powder	Sticky semisolid	Sticky semisolid	Sticky semisolid
THF-insoluble				
After crosslinking with S ₂ Cl ₂ (wt %)				
5 days	0	61	59	71
20 days	0	92	84	95
Physical appearance after crosslinking	Brittle powder	Rubbery solid, very little elongation	Rubbery solid, snaps back when stretched and released, breaks on ~100% stretching	Rubbery solid, snaps back when stretched and released, does not flow upon stretching to ~200%

^aTotal monomer concentration, 1.5 mole/liter; total volume for polymerization, 400 ml; solvent, EtCl.
^bEtAlCl₂ concentration in EtCl, 25 vol %.
^cBy using Eq. (1) for polyisobutylene.

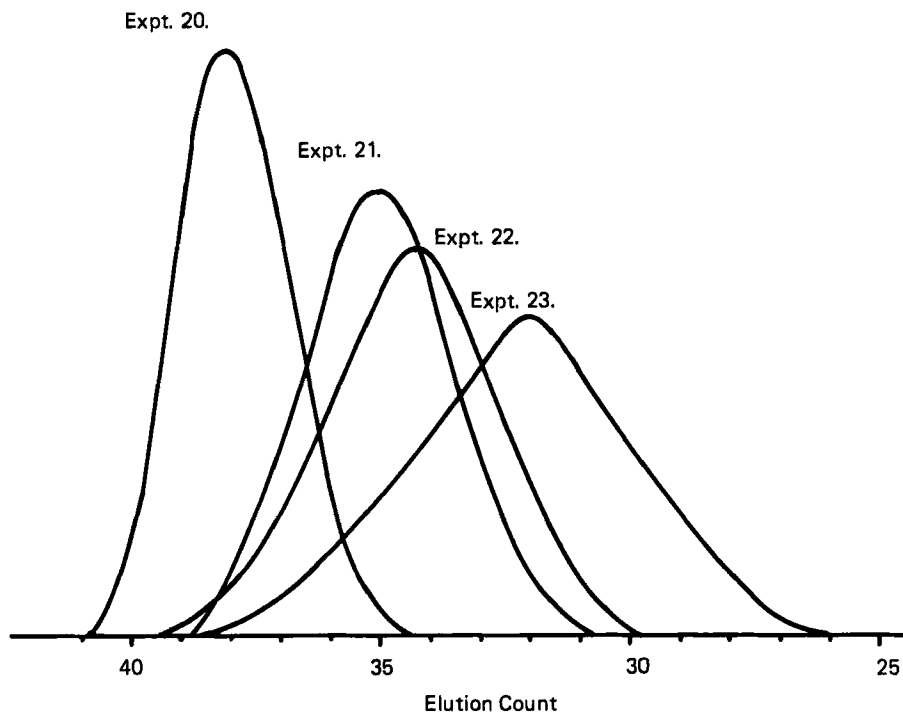


FIG. 1. Gel permeation chromatograms of poly(isobutylene-co- α -pinenes): (expt. 20) poly- α -pinene; (expt. 21) poly(isobutylene-co- α -pinene) containing 9.9 mole-% α -pinene; (expt. 22) poly(isobutylene-co- α -pinene) containing 8.2 mole % α -pinene; (expt. 23) poly(isobutylene-co- α -pinene) containing 3.2 mole % α -pinene.

α -pinene concentrations in the charge. The elution count range (30-40) indicates low molecular weight products. In the absence of appropriate calibration, molecular weight information cannot be obtained by this technique.

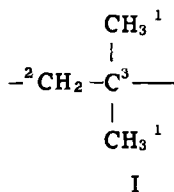
Solubility and Phase-Compatibility Studies

Blends or mixtures of polymers or heterogeneous polymers, when dissolved in a common good solvent, phase-separate into well defined layers at a characteristic concentration which depends on the nature

of the polymers and on their molecular weight. We investigated the homogeneity of our products by bringing them into dilute solution using a relatively good solvent for both polyisobutylene and poly- α -pinene, cyclohexane, and slowly concentrating them by evaporation. Thus we dissolved 2 wt % of a blend of polyisobutylene and poly- α -pinene (90.1% polyisobutylene plus 9.9% poly- α -pinene to mimic our poly- α -pinene-richest product (cf. Table 1), and the three other products described in Table 1, and slowly evaporated the solvent at room temperature. The cylinders with the solutions were constantly examined for phase separation. While the 90.1/9.9 blend of polyisobutylene/poly- α -pinene exhibited phase separation when the solid concentration rose to 9.6%, the copolymers remained optically homogeneous all the way until evaporation to dryness. Solution homogeneity under these conditions is strong indication for copolymer uniformity.

CMR Spectra of Poly(isobutylene-co- α -Pinene)

The ^{13}C -NMR spectrum of polyisobutylene showed three resonances at 29.2, 36.2 and 57.6 ppm, due to the methyl (1) methylene (2), and quaternary carbon (3), respectively:



The ^{13}C -NMR spectrum of poly- α -pinene gave a set of complicated resonances, out of which those at 25.3, 27.8, 131.0, and 139.3 ppm were assigned to gem-dimethyl carbons (1), methyl carbon (2), and to the two carbons (8 and 9) of the unsaturation. Otherwise the spectrum of the poly- α -pinene as well as the copolymers were too complex and ill resolved, respectively, for further analysis (Fig. 2).

PMR Analysis of Poly(isobutylene-co- α -Pinene)

The PMR spectra of a series of poly(isobutylene-co- α -pinenes) have been recorded and analyzed. Figure 3 shows 60 MHz PMR

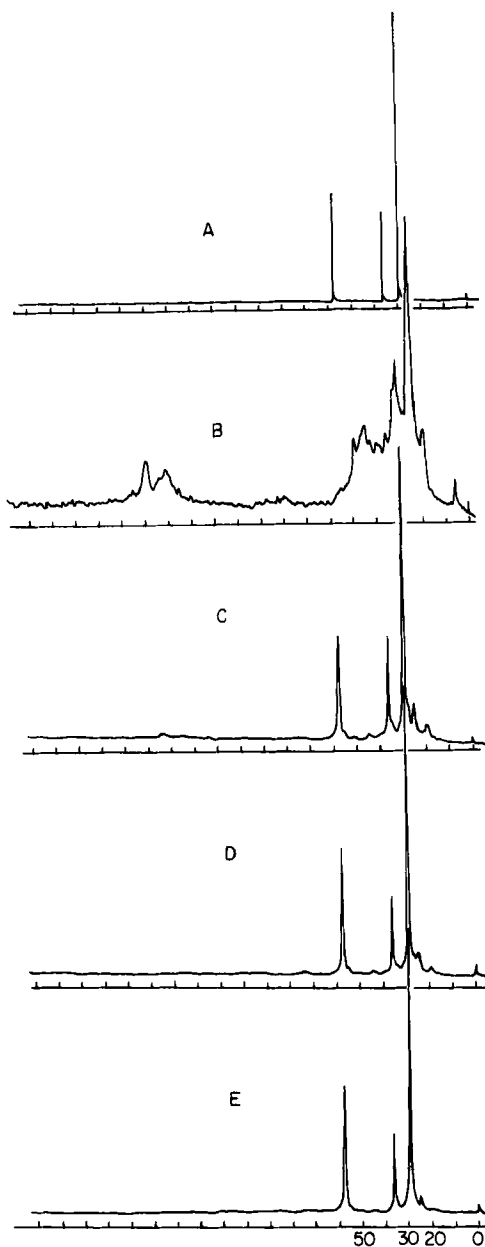
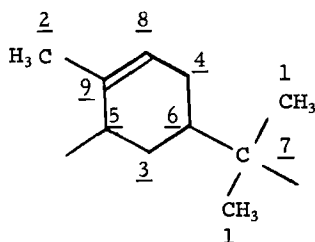


FIG. 2. CMR spectra of poly(isobutylene-co- α -pinenes): (A) polyisobutylene; (B) poly- α -pinene; (C) poly(isobutylene-co- α -pinene) containing 9.9 mole % α -pinene; (D) poly(isobutylene-co- α -pinene) containing 8.2 mole % α -pinene; (E) poly(isobutylene-co- α -pinene) containing 3.2 mole % α -pinene. In CDCl_3 , at 32°C .



II

spectra of polyisobutylene, poly- α -pinene and that of a representative copolymer containing 9.9 mole % α -pinene (Expt. 21, Table 1). A comparison of these PMR spectra with those obtained with poly(isobutylene-co- β -pinene) [1], reveals a close structural similarity between these materials. The singlet at 3.4 ppm (in parentheses) is most likely due to methoxy protons at the end of polymer chains, obtained upon quenching the polymerizations with methanol.

Similar to the findings made with the poly(isobutylene-co- β -pinene) system, the NMR spectrum of the poly(isobutylene-co- α -pinene) showed a distinct resonance (shoulder) at ~ 1.0 ppm which was absent in both the spectra of polyisobutylene and poly- α -pinene. Consequently this new resonance was assigned to isobutylene- α -pinene or α -pinene-isobutylene sequences in poly(isobutylene-co- α -pinene). To further characterize this resonance and gem-dimethyl resonances in general, we have investigated the 0.7-1.5 ppm range by high-resolution (300 MHz) NMR spectroscopy.

Figure 4 shows the methyl resonance range of a poly- α -pinene and the three copolymer samples. The resonance associated with the gem-dimethyl group in the copolymer appears as three partially resolved resonances at 1.15, 1.00, and 0.95 ppm. These results are similar to those obtained with poly(isobutylene-co- β -pinene) [1]. On the basis of these findings, we assigned the resonance at 1.15 ppm to fully crowded gem-dimethyls, i.e., isobutylene-isobutylene sequences (ii), the resonance at 0.95 ppm to uncrowded gem-dimethyls indicating an α -pinene unit that is followed by another α -pinene unit ($\alpha\alpha$), and the new resonance at 1.00 ppm to half-crowded gem-dimethyls, i.e., a gem-dimethyl group flanked by only one other dimethyl group, associated with $i\alpha$ or αi sequences. This resonance is viewed as evidence for a probably random copolymer. These assignments are shown schematically by the formula III.

The magnetic sensitivity to steric environment of gem-methyl chemical shifts has already been used to great advantage in the

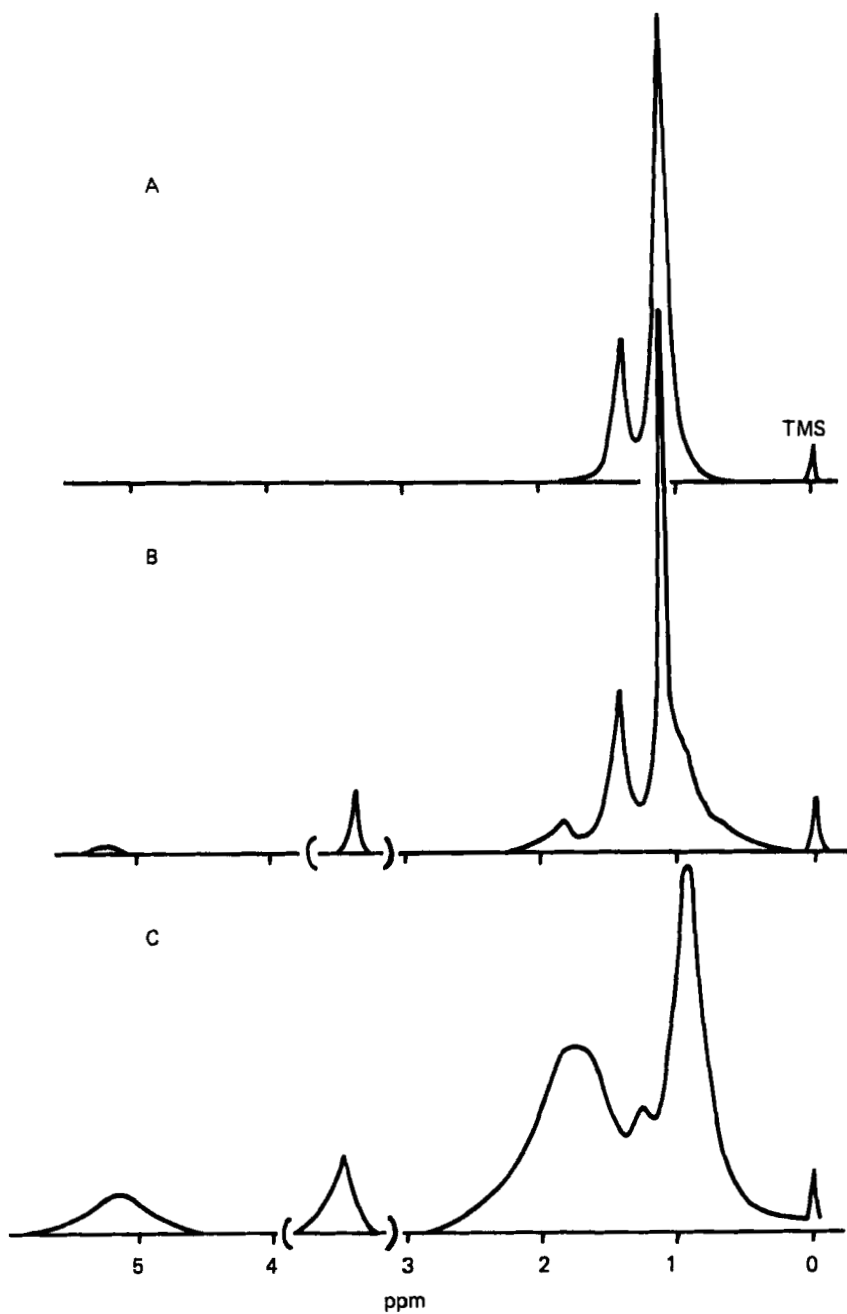


FIG. 3. PMR spectra: (A) polyisobutylene; (B) poly(isobutylene-co- α -pinene); (C) poly- α -pinene.

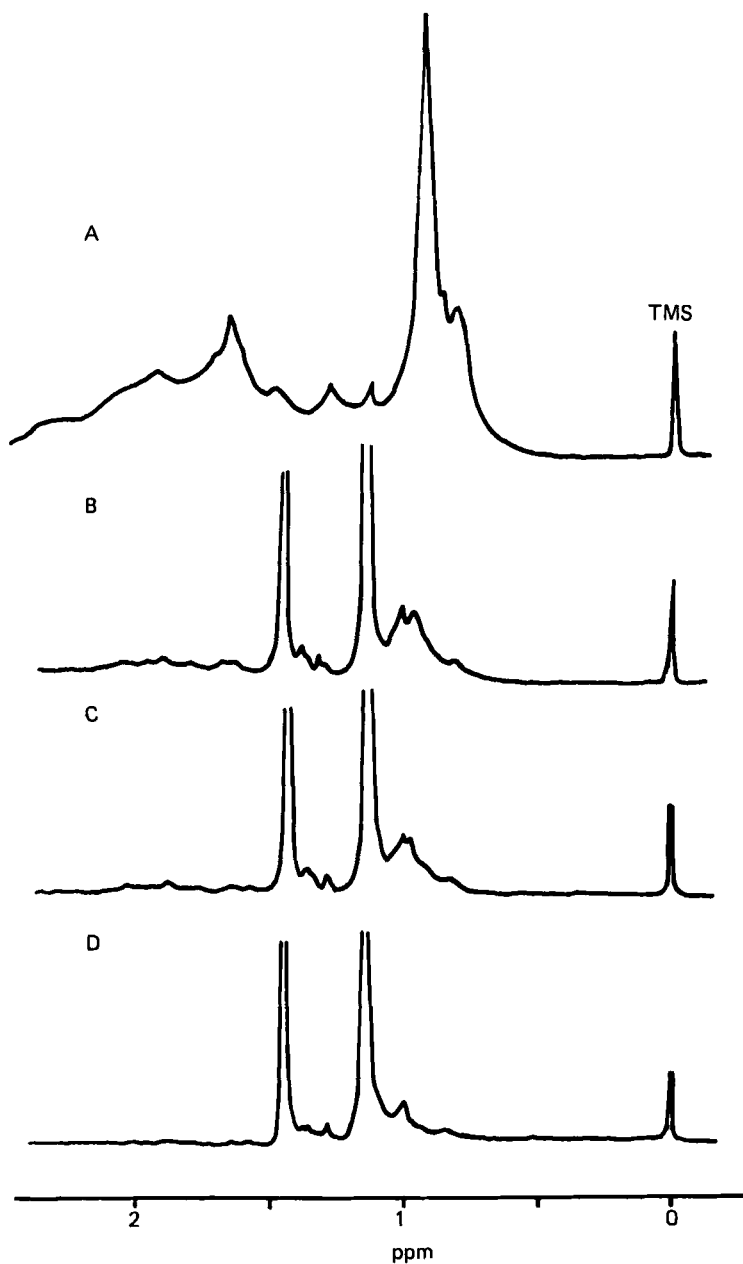
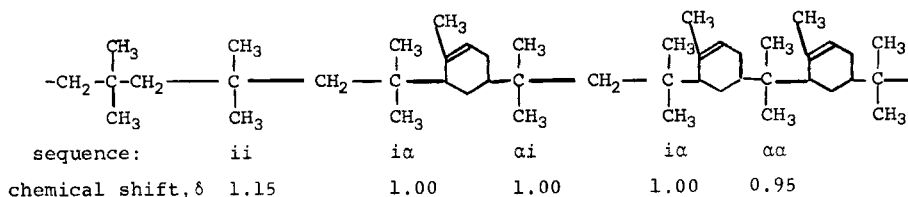


FIG. 4. High resolution PMR spectra: (A) poly- α -pinene; (B) poly(isobutylene-co- α -pinene) containing 9.9 mole % α -pinene; (C) poly(isobutylene-co- α -pinene) containing 8.2 mole % α -pinene; (D) poly(isobutylene-co- α -pinene) containing 3.2 mole % α -pinene.



III

analysis of copolymers of isobutylene [1, 3]. For example, the fully crowded gem-dimethyls resonate at 1.1 ppm, while the uncrowded gem-dimethyls in poly- β -pinene resonate at 0.8 ppm [1]. Interestingly, the gem-dimethyl group in poly- α -pinene resonates at 0.95 ppm. Possibly, increased steric compression of the gem-dimethyl groups in poly- α -pinene shifts the resonance to higher magnetic fields, i.e., to 0.95 as compared with poly- β -pinene whose less crowded gem-dimethyl groups resonate at 0.8 ppm. Unfortunately the relative proportion of uncrowded, half-crowded, and fully crowded gem-dimethyl groups in the copolymer could not be determined because of low resolution.

Determination of Reactivity Ratios

Further circumstantial evidence for the random nature of our isobutylene- α -pinene copolymers is the fact that the reactivity ratio product of isobutylene and α -pinene is close to unity, i.e., $r_i = 11.0$ and $r_\alpha = 0.09$, so that $r_i r_\alpha = 0.99$. The reactivity ratios have been determined by using the three composition data points in Table 1 and the Kelen-Tüdös equation. Unfortunately, only three compositions were available which, in spite of the satisfactory intercept definition necessary for reactivity ratio calculation by this method [7], is somewhat less than desirable for a definitive reactivity ratio analysis.

Vulcanization of Poly(isobutylene-co- α -Pinene)

The presence of unsaturation in the copolymer and the random distribution of α -pinene units in the chain was also studied by cross-linking experiments with S_2Cl_2 . Thus when copolymer samples were

dissolved in THF and S_2Cl_2 was added, 60-70% gel formed after 5 days on the shaker and almost complete gelation occurred after 15 additional days of storage at room temperature. Control samples with polyisobutylene and poly- α -pinene showed no sign of crosslinking (see Table 1). Network formation indicates unsaturation in the chain and is regarded as further evidence for the presence of randomly distributed α -pinene units in the copolymer.

CONCLUSIONS

The analysis of the data discussed above leads us to conclude that isobutylene and α -pinene can be copolymerized and that the products are probably random chains of reasonable molecular weight. The polymerizations proceed readily even at very low temperatures. According to the monomer reactivity ratios, α -pinene is difficult to incorporate into the chain which is most likely due to the internal double bond in this monomer. This situation of course is quite different with β -pinene, which is a more reactive monomer than isobutylene. It is also noteworthy that copolymer molecular weight depression (chain transfer activity) by α -pinene is much higher than that of the β isomer.

The detailed structure of the copolymer is yet unknown. On the basis of the organic chemistry of α -pinene and its homopolymerization behavior [8, 9] we have assumed, and our spectroscopic data seem to indicate, that the main contributing repeat unit is that shown above. However, it is possible that the copolymer also contains other α -pinene units which may arise by other isomerization routes.

The two main reasons Sivola and Harva [4] obtained mainly a mixture of homopolymers when they added BF_3 or $AlCl_3$ dissolved in CH_2Cl_2 to isobutylene/ α -pinene mixtures in the temperature range from -10 to $50^\circ C$ is that the monomer composition of the charge was 1:1 and that the conversion level was too high (40-44%). In view of the very low reactivity ratio of α -pinene, had the Finnish authors worked with a high α -pinene concentration in the charge and had they stopped the reaction at a reasonably low conversion, they probably would have obtained true copolymers.

ACKNOWLEDGMENTS

Partial financial support by the National Science Foundation is gratefully acknowledged. One of us (M. Nakao) appreciates leave of absence and financial support by the Arakawa Forest Chemical Company.

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Accepted by editor March 15, 1977

Received for publication April 22, 1977