

Synthesis of Phenol-Terminated Polyisobutylene: Competitive Chain Transfer Reactions

J. M. ROONEY,* *W. R. Grace & Co., Washington Research Center,
Columbia, Maryland 21044*

Synopsis

Polymerizations of isobutylene initiated by either aluminum trichloride or tin tetrachloride were conducted in the presence of alkyl phenols in both *n*-heptane and methylene dichloride solutions at temperatures between -10 and -70°C . The resultant polymers contained both unsaturated and phenolic endgroups in varying proportions dependent upon reaction conditions. Increased phenol concentrations in the polymerization medium resulted in decreased polymer molecular weights and increased phenol endgroup content. Increased reaction temperature reduced polymer molecular weights and phenol endgroup content. Chain lengths governed by ring alkylation were found to be less sensitive to polymerization temperature than those determined by other modes of chain transfer.

INTRODUCTION

Alkyl-substituted phenols are employed as antioxidants in a variety of lubricants. In an effort to increase the compatibility of the phenol groups with an essentially hydrocarbon environment, recent research has concentrated on incorporating phenols as endgroups in polyisobutylene.¹ One approach involves reacting a terminally unsaturated polyisobutylene with a phenol in the presence of a Lewis acid and a protogenic compound.² An alternative approach utilizes the phenomenon of chain transfer to phenols in the cationic polymerization of isobutylene. This reaction has been examined by Russell et al.^{3,4} for ethyl chloride solutions of isobutylene polymerized by phenol-tin tetrachloride complexes. The present work represents a study of this second approach with respect to the effects of temperature, reagent concentrations, and the nature of the solvent and initiator on the efficiency of phenol endgroup incorporation as opposed to other modes of chain breaking.

EXPERIMENTAL

Materials

Isobutylene was passed through columns of sodium-lead alloy and calcium hydride under vacuum before use. Methylene dichloride and *n*-heptane were purified by washing with concentrated sulfuric acid, dilute potassium hydroxide solution, and distilled water. These solvents were then dried over calcium chloride and calcium hydride and fractionated from calcium hydride. Phenols (Fluka), thionyl chloride (J. T. Baker, "purified"), anhydrous aluminum trichloride (J. T. Baker), and tin tetrachloride (J. T. Baker) were used as received.

* Present address: Loctite (Ireland) Ltd., Whitestown Industrial Estate, Tallaght, Ireland.

Procedure

Polymerizations were conducted under vacuum in Pyrex vessels equipped with Teflon stirring blades and syringe caps. Known volumes of solvent and isobutylene were condensed into the vessels and phenols were added through the syringe caps prior to addition of the metal halide. Tin tetrachloride was added without dilution, while aluminum trichloride was dissolved in thionyl chloride before use. Reactions were terminated after the desired time had elapsed by the addition of methanol.

Polyisobutylene was reprecipitated from tetrahydrofuran (THF) solution before drying to constant weight for the determination of percentage monomer conversion. Polymer molecular weights were estimated by differential refractive index measurements on a Waters model 244 high-pressure liquid chromatograph equipped with columns of 1000, 500, and 100 Å μ -Styragel. THF was used as the mobile phase. A gel permeation chromatography (GPC) calibration for polyisobutylene derived by Huang et al.⁵ permitted the calculation of molecular weights. The distribution of phenol within polymer samples was determined by differential UV spectroscopy on a Waters model 440 absorbance detector adjusted to a wavelength of 280 nm. Total phenol concentrations in heptane solutions of polyisobutylene samples were measured by UV spectroscopy on a Cary 14 M spectrophotometer. Infrared spectra of polymer samples were measured on a Beckman model IR4 spectrophotometer and proton NMR spectra were measured for CDCl_3 solutions on a Varian spectrometer.

RESULTS

Isobutylene was polymerized in the presence of 2-*sec*-butyl phenol by an aluminum trichloride-thionyl chloride mixture in methylene dichloride during one series of experiments and in *n*-heptane during another. A series of polymerizations in which 2,6-dimethyl phenol was substituted for 2-*sec*-butyl phenol was also conducted in methylene dichloride. Polymerizations of isobutylene involving 2-*sec*-butyl phenol and tin tetrachloride were conducted in methylene dichloride, but polymerization could not be induced in *n*-heptane solution under similar conditions.

Infrared spectra of polyisobutylenes from all systems displayed identical features. Two types of double bond could be discerned. Peaks at 895 and 1640 cm^{-1} indicated the presence of terminal gem-disubstituted olefins while peaks at 820 cm^{-1} characteristic of trisubstituted olefins were also observed.⁶ Proton NMR analyses confirmed these observations, revealing a broad singlet at $\delta = 4.8$ ppm, attributable to geminal protons on a disubstituted terminal olefin, and a peak at 5.1 ppm, assigned to the proton on a trisubstituted olefin. Peaks at $\delta = 7.10, 6.95, 6.65,$ and 6.55 ppm, ascribed to the aromatic protons in 2-*sec*-butyl phenol, were also observed.

Determinations of the relative amounts of free and bound phenol in the polyisobutylene samples were made by GPC using differential UV spectroscopy at 280 nm. Differential refractive index measurements were found to be unreliable for this purpose, as the example in Figure 1 demonstrates. Estimates of the concentration of bound phenol were made by measuring the total phenol concentration by UV spectroscopy, assuming the molar extinction coefficient to be that of the monomeric phenol (2000 l./mol cm for 2-*sec*-butyl phenol and

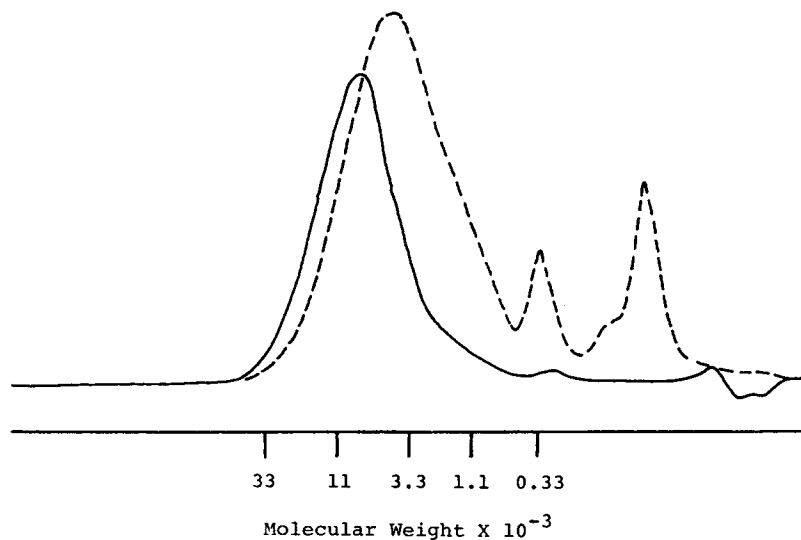


Fig. 1. Gel permeation chromatograms with UV detector trace (---) and refractive index detector trace (—) for polyisobutylene produced in methylene dichloride with $[IB]_0 = 2.4$ mol/l., $[SnCl_4]_0 = 0.10$ mol/l. and $[Ph] = 0.16$ mol/l. at -70°C .

1450 l./mol cm for 2,6-dimethyl phenol), and multiplying by the fraction of polymerically bound phenol calculated from the GPC data.

Analytical data for a series of polyisobutylenes prepared with the aluminum trichloride–thionyl chloride system are presented in Table I. The principal features of these data are (1) increased phenol concentration reduces polymer yield and molecular weight while increasing phenol incorporation; (2) the in-

TABLE I
Polymerizations of Isobutylene (IB) Initiated by Aluminum Trichloride ($AlCl_3$) in Methylene Dichloride Solution Containing 2-*sec*-Butyl Phenol (Ph)^a

T, °C	[IB], mol/l.	$10^2 \times [AlCl_3]$, mol/l.	$10^2 \times [Ph]$, mol/l.	Yield, %	\bar{M}_w	\bar{M}_n	% Phenol-capped chains
-70	2.4	4.5	0.4	88.6	23,900	11,800	2.1
-70	2.4	4.5	0.8	81.8	12,100	5,800	1.5
-70	2.4	4.5	2.0	68.4	17,200	8,400	4.7
-70	2.4	4.5	4.0	75.6	9,700	2,900	5.4
-70	2.4	4.5	8.0	55.3	6,400	2,800	19.8
-70	2.4	4.5	20.0	43.4	7,000	4,000	16.5
-50	2.4	4.5	4.0	46.9	10,200	4,400	7.5
-30	2.4	4.5	4.0	27.1	6,700	3,200	2.8
-10	2.4	4.5	4.0	13.7	5,200	2,900	2.3
-70	0.7	4.5	4.0	87.5	10,800	3,000	4.3
-70	4.1	4.5	4.0	53.8	11,400	4,000	5.1
-50	2.4	0.45	8.0	0.0	—	—	—
-70	2.4	2.3	4.0	30.7	9,500	3,900	6.6
-70	2.4	4.5	10.0 ^b	57.9	11,600	3,600	14.7
-70	2.4	4.5	5.0 ^b	65.8	12,900	4,400	8.9
-70	2.4	4.5	2.5 ^b	66.5	11,300	4,100	2.6

^a All reactions contain 0.72 mol l^{-1} $SOCl_2$ to solubilize $AlCl_3$; reactions were quenched with methanol after 15 min.

^b In these reactions, 2,6-dimethyl phenol was substituted for 2-*sec*-butyl phenol.

TABLE II
 Polymerizations of Isobutylene (IB) Initiated by Aluminum Trichloride (AlCl₃) in *n*-Heptane Solution Containing 2-*sec*-Butyl Phenol (Ph)^a

<i>T</i> , °C	Yield, %	\bar{M}_w	\bar{M}_n	% Phenol-capped chains
-70	32.8	14,000	4600	32.5
-50	49.3	14,500	7500	15.7
-30	30.8	11,400	5200	28.3
-10	23.0	8,800	4600	8.6

^a All reactions contain 0.72 mol/l. SOCl₂ to solubilize AlCl₃; [IB]₀ = 2.4 mol/l.; [AlCl₃]₀ = 4.5 × 10⁻² mol/l.; [Ph]₀ = 4.0 × 10⁻² mol/l.; reactions were quenched with methanol after 15 min.

corporation of phenol is not the principal chain-breaking reaction under any conditions; (3) reduced temperature and monomer concentration both increase polymer yields without significantly affecting molecular weight or phenol incorporation. A reaction in which 0.09 mol/l. AlCl₃ was added as a suspension in CH₂Cl₂ without thionyl chloride to 2.4 mol/l. isobutylene and 0.04 mol/l. 2-*sec*-butyl phenol in CH₂Cl₂ gave a 23% yield of high molecular weight polyisobutylene ($\bar{M}_n > 20,000$) with negligible phenol content (<1%). The high polymer molecular weight and low phenol content are attributable to the relatively low solubility of AlCl₃ in the absence of thionylchloride.

Data for polymerizations in *n*-heptane initiated by AlCl₃-SOCl₂ are listed in Table II. Polymer yields are lower and phenol incorporation greater than in comparable reactions conducted in methylene dichloride. Analyses of polymers prepared in the presence of SOCl₂ without phenols showed no evidence of chain breaking induced by the SOCl₂.

Experiments involving tin tetrachloride as the initiator, shown in Table III, displayed features similar to those involving aluminum trichloride. Polymer molecular weights and yields decreased with increasing phenol concentration. Phenol incorporation increased almost in proportion to the initial phenol concentration until approximately one-half of the polyisobutylene chains were capped with phenol. Further increases in phenol concentration only reduced

TABLE III
 Polymerizations of Isobutylene (IB) Initiated by Tin Tetrachloride (SnCl₄) in Methylene Dichloride Solution Containing 2-*sec*-Butyl Phenol (Ph)^a

<i>T</i> , °C	[Ph], mol/l.	Yield, %	\bar{M}_w	\bar{M}_n	% Phenol-capped chains
-30	0.16	97.1	5700	2530	12.0
-30	0.24	79.3	5400	1400	7.7
-50	0.08	100.0	9400	4100	11.3
-50	0.16	80.6	6400	3100	17.6
-50	0.24	95.0	8100	2800	33.1
-50	0.32	100.0	3700	1900	32.6
-50	0.40	84.8	4200	2200	47.0
-50	0.80	39.7	1800	920	26.2
-70	0.16	62.3	8900	5100	30.9
-70	0.24	64.5	5400	3200	23.8

^a [IB]₀ = 2.4 mol/l.; [SnCl₄]₀ = 0.10 mol/l.; reactions were quenched with methanol after 30 min.

the efficiency of the ring alkylation reaction. A series of experiments was conducted to determine whether postpolymerization reactions could account for the incorporation of phenol groups into the polymer chains. The results of these experiments are listed in Table IV.

DISCUSSION

Polymerizations of isobutylene initiated in the presence of phenols by either aluminum trichloride or tin tetrachloride yielded products of decreasing molecular weight as the initial phenol concentration was increased. Incorporation of phenolic endgroups, suggesting chain transfer by ring alkylation, did occur but the predominant chain-breaking reaction in all cases studied was found to result in unsaturated termini. The increased frequency of this proton expulsion reaction may be attributed to several factors: (1) the phenols may contain trace impurities which promote chain transfer by proton elimination* ; (2) free phenol molecules may act as proton transfer agents; (3) the rate of proton recapture by counterions containing the phenolate group may be enhanced by increases in total phenol concentration. Polymer molecular weights were significantly lower than those observed for isobutylene polymerizations in which chain length is governed by transfer to monomer of water,⁷ or for polymerizations conducted in the presence of phenyl chloroacetate or phenyl chloroformate⁸ which would be expected to contain impurities similar to those found in phenols.

Under certain conditions² terminally unsaturated polyisobutylene can be protonated to yield carbocations which participate in Friedel-Crafts alkylation of aromatic rings:

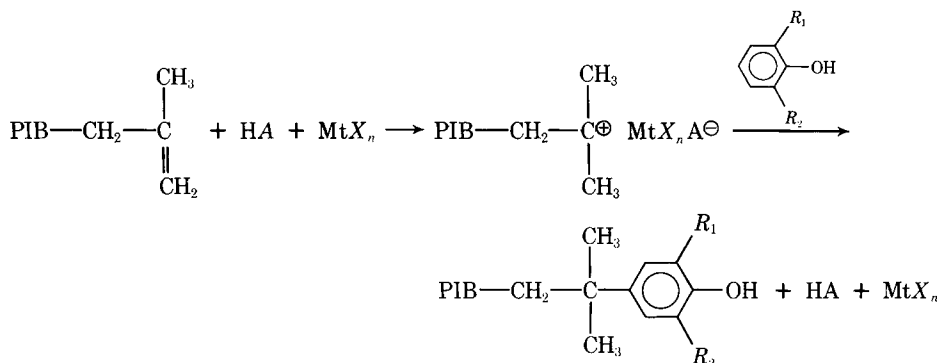


TABLE IV
Polymerizations of Isobutylene (IB) Initiated by Tin Tetrachloride (SnCl₄) in Methylene Dichloride Solution Containing 2-sec-Butyl Phenol (Ph)^a

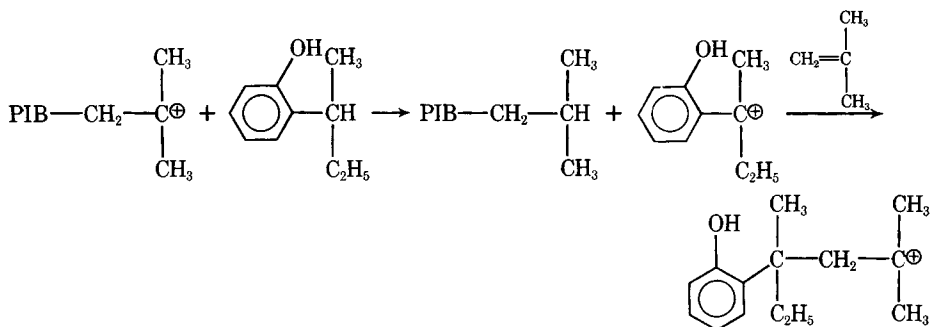
Polymerization time, min	Yield, %	\bar{M}_w	\bar{M}_n	% Phenol-capped chains
60	100.0	9,700	4500	11.0
30	100.0	9,400	4100	11.3
20	100.0	9,500	4200	14.6
10	100.0	12,200	5300	15.4

^a [IB]₀ = 2.4 mol/l.; [SnCl₄]₀ = 0.10 mol/l.; [Ph]₀ = 0.08 mol/l.; T = -50°C.

* The 2-sec-butyl phenol used was found to be 99.6% pure by GC analysis.

where MtX_n is a metal halide and HA is a protogenic molecule. However, the reaction conditions employed in the present work do not favor this reaction as the data in Table IV indicate.

Incorporation of 2-*sec*-butyl phenol through the reaction



is probably not significant since similar polymeric phenol contents are obtained for reactions involving 2,6-dimethyl phenol.

The availability of both refractive index and UV detector traces for chromatograms enables the distribution of phenols within the polyisobutylene samples to be determined. If the number-average molecular weight (\bar{M}_n) values calculated for each trace are equivalent, then the phenols are distributed uni-

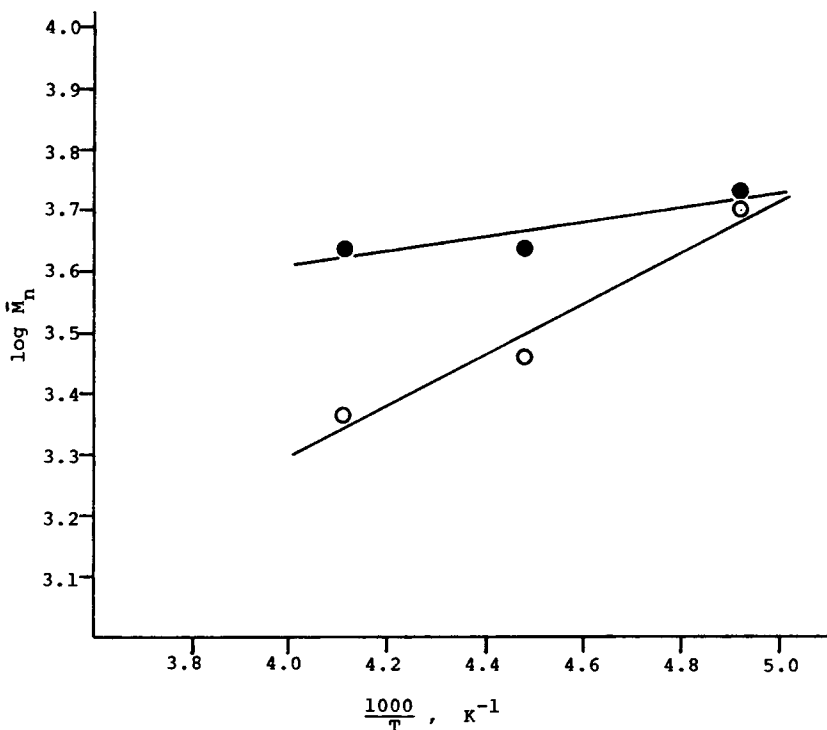


Fig. 2. Arrhenius plots for number-average molecular weights of phenol-containing (●) and phenol-free (○) polyisobutylenes produced in methylene dichloride with $[\text{IB}]_0 = 2.4 \text{ mol/l.}$, $[\text{SnCl}_4]_0 = 0.10 \text{ mol/l.}$, and $[\text{Ph}] = 0.16^\circ \text{ mol/l.}$

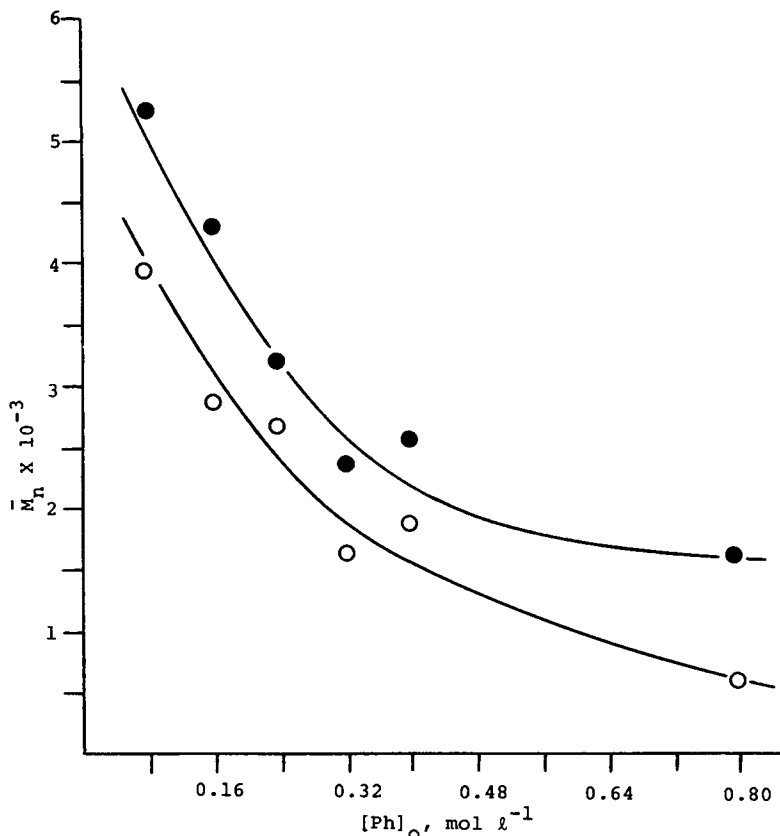


Fig. 3. Number-average molecular weights of phenol-containing (●) and phenol-free (○) polyisobutylenes as a function of initial phenol concentration in methylene dichloride with $[\text{IB}]_0 = 2.4 \text{ mol/l.}$, $[\text{SnCl}_4]_0 = 0.10 \text{ mol/l.}$ at $T = -50^\circ\text{C.}$

formly among polymer chains of all lengths. A higher value of \bar{M}_n for the UV detector trace would indicate that phenol groups were concentrated primarily in higher molecular weight polyisobutylene chains. Calculations show that the \bar{M}_n of the UV-active (phenol-containing) polymer chains is higher than that of the total polymer. In Figure 2, Arrhenius plots of \bar{M}_n for the phenol-free and phenol-containing chains within given polymer samples are presented. The chain lengths governed by ring alkylation appear to be less dependent upon polymerization temperature than those determined by other modes of chain transfer. The plots suggest that at low temperatures phenol incorporation may be the dominant mode of chain transfer in the isobutylene— SnCl_4 — CH_2Cl_2 system. Increased phenol concentration results in reductions of \bar{M}_n for both phenol-free and phenol-containing polyisobutylene chains. However, the magnitude of the difference between the respective \bar{M}_n values appears to pass through a minimum at phenol concentrations corresponding to those at which the percentage of phenol incorporation is highest, as Figure 3 illustrates.

The difference in \bar{M}_n between phenol-capped and phenol-free polyisobutylene chains within given systems may be attributed solely to differences in temperature and reaction medium effects on competing transfer processes. Alternatively, two independent propagating species may be envisioned which give rise

to different transfer mechanisms. One practical consequence of the phenomenon is that the functionality of the polymer may be improved by careful fractionation.

References

1. D. C. Edwards and J. Walker (to Polysar Ltd.), German Offen. No. 2,723,375, May 25, 1976.
2. L. Plonsker and R. E. Malec (to Ethyl Corp.), U.S. Patent No. 4,025,451, May 24, 1977.
3. R. F. Bauer, R. T. LaFlair, and K. E. Russell, *Can. J. Chem.*, **48**, 1251 (1970).
4. R. F. Bauer and K. E. Russell, *J. Polym. Sci. Part A-1*, **9**, 1451 (1971).
5. S. C. Feinberg, personal communication.
6. M. St. C. Flett and P. H. Plesch, *J. Chem. Soc.*, 3355 (1952).
7. J. H. Beard, P. H. Plesch, and P. P. Rutherford, *J. Chem. Soc.*, 2566 (1964).
8. J. M. Rooney, unpublished results.

Received September 6, 1979

Revised December 12, 1979