

Hydrogen-Peroxide-Initiated Polymerization of Isoprene in Alcohol Solutions

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SYNOPSIS

The radical polymerization of isoprene in alcohol solutions initiated by hydrogen peroxide was studied. It was found that alcohols were components of the initiated system and that their fragments with hydroxyl groups were included in every second molecule of an oligomer irrespective of the type of alcohol, of the monomer conversion, and of the oligomer molecular weight. The oligomer yields and its molecular weight were determined by alcohols through their effect upon the phase state of polymerization systems. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

The hydrogen peroxide (HP)-initiated polymerization of diene monomers is an easy and effective way of obtaining oligodienes with the end hydroxyl groups, which are the initial products for the synthesis of freeze-resistant hydrolytically stable polyurethanes.¹

The polymerization is carried out in a homogeneous system formed by adding a solvent common for diene and aqueous HP solutions. Generally these solvents are the lower aliphatic alcohols. Under production conditions the process is carried out in an isopropyl alcohol solution at 100–130°C for 3–5 h.² Such conditions give oligobutadienes with the end hydroxyl groups containing 2.2–2.8 hydroxyl groups per one molecule with a broad functionality distribution.^{3,4} The most well known of such oligobutadienes are the Poly-bd products of ARCO Chemical Company. Though such oligomers can be cured by polyisocyanates without use of low molecular cross-linking agents, the physical and mechanical properties of their vulcanizates are far from those obtained on the basis of oligodienes synthesized by

means of azonitrile initiators.⁵ The latter have average functionality close to 2 and a narrow distribution by functionality.⁶

HP is the source of the hydroxyl radicals initiating polymerization. These radicals are very active in the hydrogen abstraction reactions, which is reflected in the interaction of HP with a polymer and a solvent. The reactions of the hydroxyl radical with a polymer result in formation of branched and hence polyfunctional molecules. Also the oligomers oxidation products especially of low molecular fractions are formed, and a considerable amount of other, apart from hydroxyl, oxygen-containing groups (such as carboxyl, aldehyde, or epoxy groups) are formed in high molecular fractions. This results in extremely low efficiency of the HP initiation (0.2–0.3), compared with azonitrile initiators (0.68–0.78).⁷

The polymerization of dienes can proceed with acceptable rate already at 80–90°C. Under such conditions one can obtain oligomers with the average hydroxyl functionality close to 2, which opens prospects of obtaining elastomers with good properties. In the process of the HP-initiated dienes polymerization, a substantial role is played by the solvent. This work presents the results of our studies of the role of alcohols in this process by means of the radioactive tracer method and by the methods of functionality distribution.

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EXPERIMENTAL

Polymerization Procedure

The isoprene polymerization was carried out in glass ampoules or in metal vessels. The isoprene concentration was 3.6 mol/L, and the molar ratio of the isoprene to HP was equal to 6. The freshly distilled alcohols and the isoprene were used. The 30% HP was not purified from the stabilizer. Special experiments demonstrated that the stabilizer in HP did not effect either kinetics of the process or the yield, or the properties of the oligomers. The experiments in the glass ampoules were conducted by the standard techniques.^{8,9} The content of the ampoules was degassed by three freeze-pump-thaw cycles, the ampoules were sealed under vacuum, and then put into the thermostat preheated to 90°C. The polymerization was carried out up to about 40% conversion (for 10 h). The experiments to determine the dependence of the oligomers yield on the alcohol used as a solvent (see Table IV) were conducted in the stainless-steel autoclaves prepassivated with nitric acid and HP¹⁰ for 7 h at 90°C. In all cases the oligomers were separated through pouring the content of the ampoule (vessel) out into water. The residual HP and the alcohol dissolved in water while the oligomer and the residual isoprene collected on the water surface. After evaporation of the isoprene, the oligomer was collected and dried in a specially designed rotary set at 77°C under 10⁻³ mmHg.

Characterization

The hydroxyl groups content was determined¹¹ through acetylation by the acetic anhydride and by the reaction with the phenylisocyanate; the number-average molecular weight was determined by ebulliometry in toluene. The specific radioactivity was determined by the LS-250 Backman scintillation counter; the activity of the labeled alcohols was about 6 × 10⁴ pulses/s g.

The molecular weight distribution of the oligomers was determined by gas phase chromatography (GPC) with the use of the Waters-200 instrument; the calibration was conducted by the polyisoprene fractions. The preparative fractionation by the molecular weights was performed as in Valuev et al.¹² The distribution by the hydroxyl groups was accomplished by the method of liquid adsorption chromatography.¹³

The turbidimetric titration of the benzene oligoisoprene solution by alcohols was accomplished by means of the T-107 laboratory photoelectric titrator in a cell 2 cm wide.

RESULTS AND DISCUSSION

Functionality of Oligoisoprenes Obtained in Solutions of Labeled Alcohols

In oligomers obtained in solutions of the alcohols labeled ¹⁴C, the content of the hydroxyl groups by acetylation and specific radioactivity have been determined. By the given molecular weight and content of the hydroxyl groups, one calculated the hydroxyls functionality \bar{f}_n^{ac} , which includes primary and secondary hydroxyl groups determined by the acetylation method. By means of specific activity the functionality was found by the label \bar{f}_n^* , which indicates amount of alcohol molecules in the oligomer molecule. The results are presented in Table I.

The following regularities can be derived from the data of Table I.

1. Fragments of alcohols are incorporated in the oligomers. Their content is almost the same for all the oligomers irrespective of the alcohol used as a solvent and of the monomer conversion and is equal to about one fragment per 2 oligomer molecules (\bar{f}_n^* is close to 0.5).
2. Functionality by primary and secondary hydroxyl groups in the oligomers obtained in solutions of the primary (methyl, ethyl) alcohols is close to 2 and that of the secondary (isopropyl) alcohol is close to 1.5.

Although for a series of specimens there are marked deviations from those values, we consider the general regularities to be fairly reliable. That was substantiated by the results of determining (by other methods) hydroxyl groups in oligodienes obtained with HP present. Earlier¹⁴ the content of hydroxyl groups in oligobutadienes synthesized in solutions of the isopropanol was determined by chemical methods. The content of the tertiary hydroxyl groups in oligomers was found, and functionality equal to 0.50 ± 0.06 was calculated both by difference between the content of the hydroxyl groups determined by the reaction with the phenylisocyanate and that determined by the reaction of acetylation. The content of the secondary hydroxyl groups in the oligobutadiene synthesized in the ethanol solution was determined by ¹H-NMR spectroscopy. That content made up 22% of the total amount of the hydroxyl groups,¹⁵ that is, every fourth hydroxyl group belonged to the fragment HOCH(CH₃)—. The recent study of the hydroxyl groups of the oligoisoprenes by ¹H-NMR spectroscopy through treating them by the trichloroacetylisocyanate has given the results¹⁶ shown in Table II.

Table I Functionality of Oligoisoprenes Obtained in Solutions of Labeled Alcohols^a

Alcohol	Monomer Conversion (%)	Molecular Weight (M_n)	Average Functionality	
			By Acetylation Results f_n^{ac}	By label f_n^*
Methyl	25	1850	2.03	0.46
	—	2100	2.06	0.45
	50	1700	2.04	0.47
	54	1850	2.07	0.60
	72	1900	1.96	0.74
Ethyl	25	2150	1.94	0.38
	40	2100	1.95	0.35
	45	2400	1.94	0.35
	74	2950	2.01	0.45
Isopropyl	38	4600	1.47	0.43
	40	1700	1.59	0.51
	—	2250	1.52	0.51
	60	4700	—	0.47
	74	4050	1.67	0.44
	80	2250	1.77	0.52

^a Conditions of polymerization: isoprene concentration 3.6 mol/L, initiator concentration 0.6 mol/L, polymerization temperature 90°C, polymerization time 10 h, in glass ampoules.

The data of Table II show that fragments of the alcohols retain the hydroxyl groups when entering the oligomers, but in this case the hydroxyl groups of the primary alcohols turn into the secondary ones (with the exception of the methanol), and those of the secondary alcohols turn into the tertiary ones. The deviation from the data of Table I is explained by the procedure difficulties in determining the content of the hydroxyl groups of different classes by the intensity difference caused by superimposing the signals of different protons after the hydroxyl groups are treated with the trichloroacetylisocyanate.

Table II Hydroxyl Groups Content in Oligoisoprenes Synthesized in Alcohol Solutions^a

Alcohol	Fraction of Hydroxyl Groups (%)		
	Primary (alcoholic to include)	Secondary	Tertiary
Methyl	100 (27.6)	—	—
Ethyl	77.3 (—)	22.7	—
Propyl	69.3 (—)	30.7	—
Isopropyl	62.2 (—)	—	37.8

^a Determined by ¹H-NMR spectroscopy after the hydroxyl groups are treated by the trichloroacetylisocyanate.

Figure 1 presents the functionality dependence by the hydroxyl groups determined by acetylation and by the label of fractions of the oligoisoprenes of various molecular weights synthesized in solutions of three alcohols. It is obvious that the functionality by label for all the oligomers (except for the low molecular fractions of the oligomer obtained in the methanol solution) is close to 0.5 and does not change through the whole range of the molecular weights.

Table III gives molecular characteristics of the oligoisoprenes synthesized in solutions of the primary alcohols.

Table III shows that the oligoisoprenes obtained in the solutions of the primary alcohols at moderate conversions of the monomer contain a considerable fraction of the bifunctional molecules and the average functionality is close to 2.

Methods by which Alcohol Fragments Enter Oligomer Molecule

The presented facts indicate that unlike the well-known cases¹⁷ in the given system, the solvent attaches to the polymer in such an amount that cannot be explained by the chain transfer onto the solvent with the subsequent initiation of the polymerization by the formed radical. One could assume that the

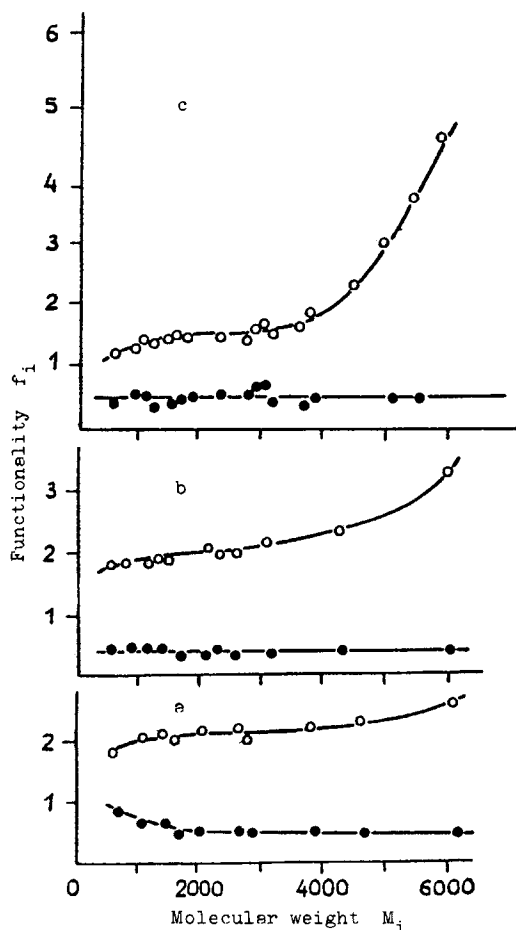
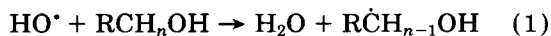
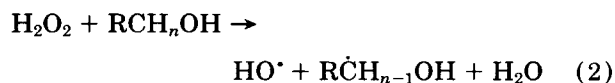


Figure 1 Relation of functionality in hydroxyl groups determined through acetylation (1) and in labels (2) of oligoisoprene fractions synthesized in the medium of (a) methyl, (b) ethyl, and (c) isopropyl alcohols against the molecular weight of fractions.

alcohol radicals are formed by the reaction of abstraction of the hydrogen atom from alcohol by the hydroxyl radical:



In this case one should expect different content of the alcohol fragments in the oligomers obtained in the solutions of various alcohols such that the reaction rate constants (1) differ greatly for the methyl, ethyl, and isopropyl alcohols to give 0.64 ± 0.05 , 2.40 ± 0.08 , and $3.30 \pm 0.15 \times 10^9 \text{ L}/(\text{mol s})$, respectively, at 23°C .¹⁸ In addition, throughout the process of polymerization, the functionality by alcohol fragments remains constant through the whole range of conversions. We suggest that the alcohol radicals incorporate with the oligomer composition at the initiation stage, and due to that the functionality by label remains constant and equal to 0.5. It occurs in the case of the stoichiometric reaction between HP and the alcohol, which results in the α -alcohol and the hydroxyl radicals:



The most probable way is a decomposition of the initially formed complex between the alcohol and HP. High excess of the alcohol in the polymerization system ensures constancy of the complex composition and the way of generating the initiating radicals by reaction (2) under all conversions. Probable structure of the alcohol-HP complexes is discussed in various studies.^{8,19}

In fact, the strength of the HO-OH bond is 48 Kcal/mol,¹⁰ which makes the homolytical decomposition of HP at $80\text{--}90^\circ\text{C}$ very slow. At these temperatures the polymerization of dienes progresses in a noticeable way. Activation energy of the HP decomposition in the solvents, i.e., which alcohols to include, is twice as low and equal to 20–25 Kcal/mol.⁸ Therefore in a solvent, HP is consumed along a mechanism that differs from the homolytical decomposition, as accepted in the majority of papers dedicated to the polymerization under the HP effect. That is how Walling²⁰ comments about the problem:

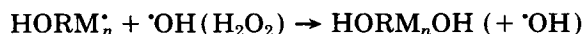
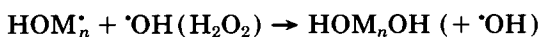
Table III Molecular Characteristics of Oligoisoprenes Synthesized in Solutions of Primary Alcohols^a

Alcohol	Molecular Weight Distribution			Distribution by Functionality (mol %)				Σf_i
	M_w	M_n	M_w/M_n	Mono-	Bi-	Tri-	Tetra-	
Methyl	3670	1580	2.3	5	82	12	1	2.09
Ethyl	3080	1650	1.9	3	83	12	2	2.13
Propyl	3440	1960	1.8	7	87	6	—	1.99

^a For the condition of polymerization, see Table I.

“So far that $D(\text{OH-OH})$ at gas phase is equal to 54 Kcal/mol the radical formation presents a pseudomonomolecular process wherein a solvent takes part in some way.”

With this initiation method one should expect the correlation of the alcoholic and peroxide hydroxyl groups in an oligomer to be 1 : 1, as it is observed, for example, in the case of initiating the butadiene polymerization by the cyclohexanol peroxide (where relation of the hydroxyl and carboxyl groups is 1 : 1).²¹ In our case this relation is 1 : 3 (with no chain transfer reaction), which indicates another mechanism of the chain termination than recombination of the macroradicals. Here two ways are possible: chain termination by the primary hydroxyl radicals or chain transfer onto the initiator-HP:



In case of polymerization in the alcohol solutions, the oligomer separates as a liquid phase. Thus when the macroradical gets a certain length it coils into a compact coil insoluble in the polymerization system, i.e., in fact the heterophase polymerization takes place. In this case the macroradicals termination by their recombination involve difficulties, and the chain termination is accomplished mainly by the primary radicals of the initiator diffusing into a molecular coil.²² The bulky alcohol radicals cannot compete with the hydroxyl radicals for the rate of diffusion into a coil, in consequence of which only the hydroxyl radicals of HP enter practically the oligomer when the chain is terminated. The indirect evidence in favor of that suggestion is the fact that in the oligomers obtained in the methanol solution the functionality by alcoholic fragments in the low molecular fractions comes close to 1 [Fig. 1(a)]. It looks like there is a diffusion of the compact radicals CH_2OH into the fairly loose coils formed by the short chains of the macroradicals, and these radicals can terminate a certain portion of the macroradicals. With the increase of the molecular weight of the fractions, the functionality drops to 0.5 and remains like that up to high molecular fractions.

Effect of Alcohol Solvency on Oligoisoprene Functionality

From that mentioned above it is evident that in the polymerization system under study the alcohol is

not just a solvent common both for diene and HP but practically a component of the initiating system. However, the role of the alcohol is not restricted solely to that. Studies^{2,23} have emphasized the influence of the alcohol on the phase state of the system, on its role as a “nonsolvent” of the oligomer, and hence on the yield and the molecular characteristics of the latter. We have investigated this influence more in detail.

We evaluated the relative dissolving capacity of the lower aliphatic alcohols (and acetone for comparison) through the turbidimetric titration of the oligoisoprene benzene solution with concentration up to 6 g/dL. The oligomer with molecular weight $M_n = 2200$ and the functionality by the primary hydroxyl groups $f_n = 1.75$ was obtained in the solution of the isopropyl alcohol. The curves of the turbidimetric titration are given in Figure 2. The dissolving capacity of the alcohol was determined as a relation of the alcohol volume at the curve bending point to the oligomer solution volume, i.e., as volume of the alcohol necessary for precipitation of 1 volume of the oligomer solution. Despite a conventional selection of the specimen, Figure 2 gives a clear picture of the relative capacity of the alcohols to dissolve the oligomers.

Table IV presents the yield and characteristics of the oligoisoprenes obtained in the solutions of a series of the alcohols and the acetone.

The processing of the results permitted us to determine the correlation between the dissolving capacity of the alcohol and the oligomer yield (correlation coefficient $r = 0.760$) and between the dissolving capacity and the molecular weight ($r = -0.702$). Though the correlation coefficients are

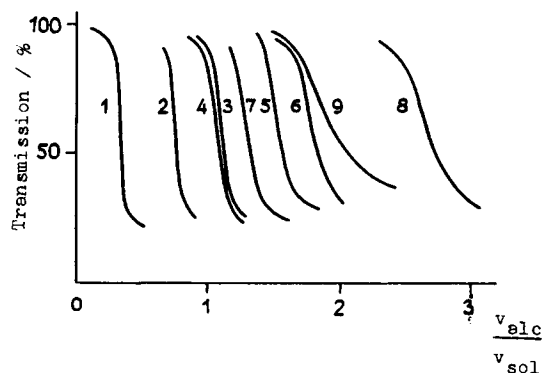


Figure 2 Curves of turbidimetric titration of a benzene oligoisoprene solution by alcohols: (1) methyl, (2) ethyl, (3) propyl, (4) isopropyl, (5) *n*-butyl, (6) isobutyl, (7) *sec*-butyl, (8) *t*-butyl, and (9) acetone.

Table IV Yield and Functionality of Oligoisoprenes Obtained in Alcohol Solutions^a

Alcohol	Solvency	Yield (%)	Molecular Weight, M_n	Functionality
Methyl	0.35	31.6	1780	1.90
Ethyl	0.75	31.9	1980	1.99
<i>n</i> -Propyl	1.09	37.0	1710	1.94
iso-Propyl	1.07	39.7	1770	1.55
<i>n</i> -Butyl	1.52	45.5	1365	1.85
iso-Butyl	1.75	34.8	1510	1.60
sec-Butyl	1.28	34.9	1420	1.52
tert-Butyl	2.66	42.3	1440	1.62
Acetone	1.83	28.5	1620	1.51

^a conditions of polymerization: isoprene concentration 3.6 mol/L, initiator concentration 0.6 mol/L, polymerization temperature 90°C, polymerization time 10 h, in the stainless-steel vessels.

not high, their values indicate the significant correlation of the above values. The criterion is the value of probability of the random arrangement of variables that makes < 5% for the determined correlation coefficients (the probability values are determined by Table C given in the study by Tailor.²⁴ The increase of the oligomer yield along with the improvement of the dissolving capacity of the alcohol we relate to the improvement of the mutual compatibility of the polymerization system components that facilitates their interaction. The decrease of the molecular weight occurs due to facilitation of the chain termination by the primary radicals or by the chain transfer to HP in more homogeneous solution.

The results of determining the functionality of the oligoisoprenes (Table IV) produced in the metal equipment generally agree with the data given above. The oligomers functionality determined by the acetylation data is close to 2 for oligomers obtained in solutions of the primary alcohols (with exception of the isobutanol) and to 1.5 for the oligomers obtained in solutions of the secondary (isopropyl, sec-butyl) alcohols and *t*-butyl alcohol as well as of the acetone.

CONCLUSION

To obtain oligomers bifunctional by the primary and secondary hydroxyl groups necessary for the synthesis of the polyurethane materials with good physical and mechanical properties, one should use only the primary alcohols and should conduct the polymerization at moderate (up to 100°C) temperatures to exclude the chain transfer reaction.

During the polymerization of the dienes effected by HP, the alcohols act not only as a common solvent of the diene and HP but produce a complex effect on all the stages of the polymerization process both through the chemical interaction with the initiator and due to the change of the phase equilibrium in the system that includes the formed oligomer.

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