

On the Miscibility of Liquid Polybutadienes

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ABSTRACT: The miscibility of a new type of liquid polybutadiene and dihydroxypolybutadiene with various organic compounds was examined. The aim was to collect data which could be used in the evaluation of the role of miscibility in polyurethanes prepared from this new polymer. Qualitative tests using the cloud-point method were made in the temperature range from laboratory conditions up to 140°C. Results were put on a common basis by the solvation equation and some characteristics derived from the electrostatic potential. Marked differences in the miscibility behavior between pure and hydroxyl-terminated polybutadiene with hydroxyl compounds were revealed. The presence of only two hydroxyl groups in a relatively long hydrocarbon chain may thus affect properties of the molecule. Polar molecules are not, in general, miscible with polybutadienes. Polarity may be balanced and miscibility enhanced by supporting π -electron-interaction capabilities, H-bond basicity, or a sufficiently long low-polar part of a partner molecule. Other ways of improving miscibility is the nonsymmetrical placement of polar groups in the molecule structure. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1628–1635, 2000

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INTRODUCTION

Liquid polybutadienes containing hydroxyl (or isocyanate or amine) groups may serve as raw materials for special polyurethanes.^{1,2} Polybutadiene-based polyurethanes should have very good hydrolytic resistance, low-temperature properties, and elasticity. These properties result from the structure of the polybutadiene backbone. Compared to the traditional and widely used polyurethane polymers—polyethers and polyesters, polybutadiene is much less polar and much more hydrophobic. Nonpolarity, however, may also cause problems. Other components of polyurethane composition—*isocyanates, chain extenders, and crosslinking agents*—are usually polar. Miscibility of polybutadiene-based polymers with these compounds may be poor. Structure of

the final product may thus be much more dependent on the initial liquid mixture and poor miscibility of the initial components may result in deterioration in the properties of the cured material.

It is well established that polyurethanes possess a microphase-separated structure.^{1–3} It consists of soft segments, made from the initial polymeric component, and hard segments, formed by the isocyanate, chain extender, and crosslinker. This microheterogeneous structure is thought to be the cornerstone of specific mechanical properties of polyurethanes.

Studies on the polyurethane microstructure have usually been focused on the examination of the structure itself. Relatively little attention has been paid to the detailed relations between the structure and properties of polyurethanes, particularly in the area of polybutadiene polyurethanes. For example, although the microphase separation in the final polyurethane material is thought to be desirable, it is not fully understood how this separation is connected with the misci-

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bility of the initial mixture and whether and how much the possible incompatibility in the initial stage should be decreased. There are also opinions that poor miscibility is of no importance in systems capable of chemical reactions.

The most important published information on the phase behavior in polybutadiene polyurethanes are now briefly reviewed: Schneider and Matton⁴ found worse mechanical properties of polybutadiene-based polyurethanes compared to the polyether- or polyester-based products. As one of the causes, they identified the poor adhesion of the polybutadiene matrix to the phase-separated hard-segment domains.

Brunette and coworkers⁵ confirmed nearly complete phase separation in polybutadiene polyurethanes due to the high incompatibility of the soft and hard segments. Xu et al.^{6,7} tackled the problem of miscibility in the initial mixture, observed the evolution of the phase separation during curing microscopically, and presented a model of the phase structure of the reacting mixture.

Bengtson and coworkers⁸ tried to restrain the poor initial compatibility by preparing polybutadiene polyurethanes from solution. Solution-prepared products possessed better mechanical properties than those of polymers prepared in bulk.

Xu et al.⁹ found even supramolecular structures formed, in their opinion because of poor miscibility of the initial components. They claimed these structures to be important for the mechanical properties but without further explanation. Speckhard and Cooper¹⁰ analyzed in detail the tensile properties of polybutadiene-based polyurethanes and stated that poor miscibility of polybutadienes with other components is one of the causes of the worse tensile properties which these products have compared to traditional materials.

Although much work has been done in investigating the structure of polybutadiene-based polyurethanes and their properties, our knowledge is still limited. The conclusive statement about the role of the miscibility in initial composition, its relation to the phase structure of the cured product, and its influence on the mechanical properties is still missing.

A new type of liquid polybutadiene, prepared by anionic polymerization, is being produced by the Kaučuk Co.¹¹ (Kralupy n. Vlt. Czech Republic) under the trade name KRASOL. This article presents the first results of our study aimed at the investigation of the miscibility role of polyurethanes prepared from this new polymer.

It was the purpose of the present work to collect a sufficiently large amount of information on the miscibility of liquid polybutadiene and on the possible causes. A number of compounds were studied by a simple miscibility test. The compounds differed in their interaction propensity and the results enabled us to discuss the miscibility behavior of liquid polybutadienes in terms of intermolecular interactions.

EXPERIMENTAL

Our main goal was of surveying the miscibility of liquid polybutadienes at laboratory temperature using a relatively large set of testing compounds. Binary mixtures composed of the liquid polybutadiene and the other component (see below) were prepared by thorough hand-mixing in a plastic container. Compounds which are solid at the laboratory temperature were weighted into the polybutadiene and liquefied by heating several degrees over their melting points. The mixture (about 10 mL) was poured into the test tube. Clear (nonclouded) mixtures were considered to be miscible.

Test tubes with cloudy, opaque mixtures, considered as nonmiscible, were subjected to a supplementary test to determine whether miscibility is achieved on heating. The tube was placed into a silicone bath and heated at most to 140°C. The sensor of the digital thermometer was immersed into the mixture during heating and served also to stir it. The disappearance of turbidity was watched for. The temperature of when the mixture became clear was also noted. The test tube was then taken out of the bath and let to cool in air to compare the cooling and heating behavior. The temperature of making the liquid turbid again was noted as well. The difference of the two temperatures was not greater than 1°. The heating rate should be similar to the rates which can be expected, in practice, for instance, in polyurethane hot-curing or self-heating by the reaction heat. The heating rate in our experiments was 5–10°C/min.

The whole procedure was tested on the phenol-water mixture for which also the phase diagram is well known. Even fairly good quantitative agreement was found (maximum error was about 11%).

One component of each mixture was either liquid pure polybutadiene KRASOL LB or liquid hydroxyl-terminated polybutadiene KRASOL

LBH. KRASOL LB is polybutadiene with M_n ranging from 2000 to 3000, about 60% of the 1,2-(vinyl) unit, and about 25% of 1,4-*trans* and about 15% of 1,4-*cis* structural units. KRASOL LBH differs in the presence of one secondary hydroxyl group (more precisely, the 2-hydroxypropyl group) at each end of the linear chain.

Samples were supplied by the Kaučuk Co. together with the following specifications: KRASOL LB: $M_w = 2608$, and $M_n = 2225$. KRASOL LBH: $M_w = 2610$, $M_n = 2310$; OH content 0.765 mmol/g; $f_2 = 91.4\%$, and $f_1 = 7.5\%$, and $f_0 = 1.1\%$ (fractions of bi-, mono-, and nonfunctional chains, respectively). The producer determines the molecular weight by GPC; OH content, by standard acetylation titration; and functionality, by HPLC.

The second component was either a chain extender or a crosslinker used in the polyurethane industry or one of the model organic compounds which differed in their structures and thus in their capabilities of intermolecular interactions. Extenders and crosslinkers were supplied by Kaučuk as samples of the standard products used there and were dried by distilling off water. The other compounds were either from Lachema (Brno, Czech Republic) or Fluka (Prague, Czech Republic) and were of "purum" degree at least. Ethanol, formamide, and dimethylformamide were dried by standard procedures and stored over molecular sieves. 1- and 2-Propanol were purchased anhydrous. Other substances were used as freshly received.

The mixtures contained from 10 to 90% (by weight) of polybutadiene, the rest being the other component. Nine mixtures were prepared for each "polybutadiene-second component" pair by 10% steps. All percentages given in this work are by weight.

RESULTS

The purpose of this study was to get a wide general picture on the miscibility behavior of liquid polybutadienes and its possible causes in terms of intermolecular interactions. Results of the experiments are presented qualitatively in Table I. Miscibility is rated according to three levels: The first level (marked "+" in Table I) means that all the mixtures were miscible at laboratory temperature (about 20°C). The second level (marked "p" in Table I), that is, partial miscibility, means that some mixtures were not miscible at laboratory temperature but became miscible by 140°C. The

Table I Results of Miscibility Tests Performed with Binary Mixtures (Concentrations 10–90% by Weight) Containing Polybutadienes KRASOL

Second Component	KRASOL	
	LB	LBH
Ethanol	0	0
1-Propanol	0	+
2-Propanol	0	+
1-Butanol	p	—
1-Pentanol	p	—
1-Hexanol	p	—
1,4-Butanediol	—	0
2,3-Butanediol	—	0
1,5-Pentanediol	—	0
1,6-Hexanediol	0	0
1,8-Octanediol	0	0
Triethanolamine	0	0
Triisopropanolamine	+	+
Ethyleneglycol	—	0
Glycerol	—	0
Dipropylene glycol	0	0
2-Ethyl-1,3-hexanediol	—	p
1,2-Hexanediol	—	p
1,2-Octanediol	—	+
Pentane	+	+
Hexane	+	+
Cyclohexane	+	+
Decane	+	+
Hexadecane	—	+
Toluene	+	+
Diethylether	+	+
Acetone	+	+
Ethyl acetate	+	+
Castor oil	p	+
Formamide	0	0
Dimethylformamide	0	0
Aniline	0	0
Pyridine	+	+
1-Nitropropane	p	+
Tetrachloromethane	+	+
Chloroform	+	+
Dichloromethane	+	+

(+) Full miscibility at laboratory temperature; (p) partial miscibility; (0) nonmiscible up to 140°C (or boiling point); (—) not determined.

last level (marked "0" in Table I) means that all mixtures were nonmiscible even at 140°C (or at the boiling point of the second component if this is lower than 140°C).

Some additional comments on the experimental results follow: Demixing temperatures of all

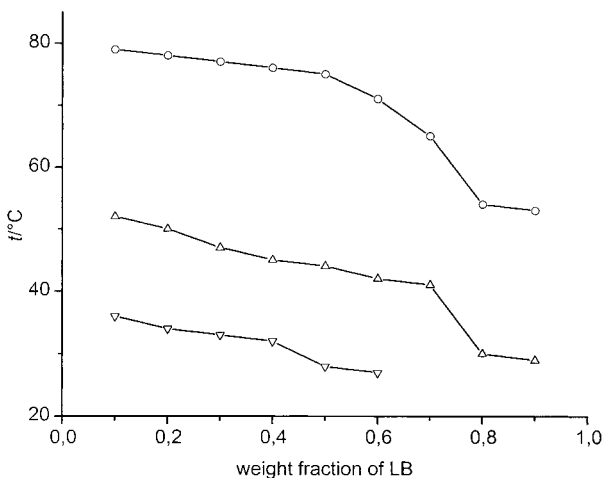


Figure 1 Sketches of the phase diagrams. Liquid polybutadiene KRASOL LB with (○) 1-butanol, (△) 1-pentanol, and (▽) 1-hexanol. Mixtures with 1-hexanol containing 70% and more LB are miscible at laboratory temperature.

mixtures of KRASOL LB with castor oil were about 112°C (in this case, the cloudiness disappears or appears between 108 and 115°C, not suddenly).

Mixtures of KRASOL LB with 1-nitropropane containing excess (>50%) of KRASOL were miscible at laboratory temperature. Demixing temperatures of the other mixtures were slightly higher, namely, 28°C (50 and 40%), 29°C (30%), 31°C (20%), and 32°C (10%).

Although it was not the goal of this study to measure exact shapes of the phase diagrams, the results enable one to draw approximate shapes of the diagrams for partially miscible mixtures. They are called sketches and are presented in Figures 1 and 2 for some mixtures (most of the other mixtures were either completely miscible or completely nonmiscible in the area of interest; thus, no phase diagram can be drawn anyway). Figure 1 shows differences in the miscibility behavior with (nonfunctional) polybutadiene in a homologous series of *n*-alcohols and Figure 2 illustrates the similar behavior of dihydroxypolybutadiene with partially miscible diol.

DISCUSSION

The phase behaviors of KRASOL LB and LBH are different in mixtures with hydroxyl-containing compounds, which are of special interest for polyurethane applications. The presence of only two

hydroxyl groups in a relatively long hydrocarbon chain may thus influence the properties of the molecule. The polymerization degree of KRASOL is about 50; thus, the polybutadiene chain consists of about 200 carbon atoms.

KRASOL LB behaves as a typical nonpolar hydrocarbon. KRASOL LBH is slightly polar due to the hydroxyl groups. The step change from its total nonmiscibility with ethanol to the complete miscibility with 1-propanol is rather surprising. Gradual improving of miscibility, as in the case of mixtures of KRASOL LB with higher alkanols (Fig. 1), could be expected.

Beginning with propanol, KRASOL LBH is miscible with alcohols. However, it is not miscible with analogical diols which are more polar. In the linear α,ω -alkanediol series, even the C₁₀ chain is not sufficient for the miscibility with KRASOL LBH. KRASOL LBH is miscible even with short (and nonpolar) alkanes.

Results obtained with alkanols and alkanediols suggest that relatively highly polar compounds (for instance, alcohols) may be more miscible with liquid polybutadienediol if they are able to form some probably "micellar" structures with their polar ends located around or connected to the polybutadiene hydroxyl groups and nonpolar main chains placed along the polybutadiene chain. Thus, for instance, 1-propanol is miscible with KRASOL LBH while 1,6-hexanediol or 1,8-octanediol are not and 2-ethyl-1,3-hexanediol is miscible with KRASOL LBH only in dilute mixtures (see also Fig. 2).

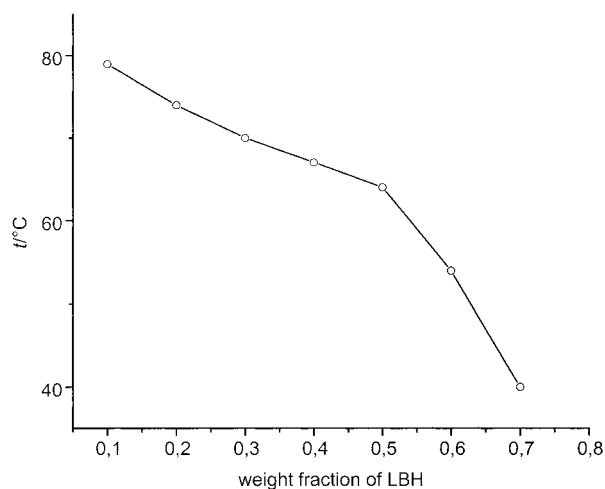


Figure 2 Sketch of the phase diagram. Liquid dihydroxypolybutadiene KRASOL LBH with 2-ethyl-1,3-hexanediol. Mixtures containing 80% and more LBH are miscible at laboratory temperature.

This speculation was confirmed by experiments with 1,2-alkanediols. 1,2-Hexanediol is partially and 1,2-octanediol is completely miscible with KRASOL LBH. The miscibility limit for 1,2-hexanediol at laboratory temperature is about 20%.

The phase diagrams sketched in Figures 1 and 2 are nonsymmetric and represent the common behavior of partially miscible mixtures of KRASOL LB and LBH: The second component is much more soluble in KRASOL than is KRASOL in the second component. It is therefore much easier to place a small amount of the second (low molecular) component into the polybutadiene matrix than vice versa. The phase diagram skewness is a phenomenon well known from the polymer solutions.

When the content of polybutadiene increases, the mixing-demixing temperature changes with the composition slowly up to 40–70% composition (see Figs. 1 and 2); then, a steep decrease is observed, and in Figure 1, another slow change follows again. Although in the latter case some error of the used experimental procedure cannot be excluded, the fact that this (second) slow change was observed for several mixtures at different temperatures suggests that it has some real cause. Probably, in mixtures with small amounts of a partially miscible, low molecular weight compound, only slight (relative to the mixtures with higher amount of the second component) heating is needed for some molecular rearrangement resulting in a miscible mixture.

Because of the differences in the molecular weight of polybutadiene and chain extenders or crosslinking agents, real polyurethane mixtures usually contain a high weight excess of polybutadiene. Actual content is dependent on the particular extender/crosslinker and application but it usually makes up no more than several weight percent (in the case of longer extender/crosslinker, for instance, dipropylene glycol or castor oil, several tens percent) from the weight of polybutadiene. Therefore, we checked the miscibility of some systems with high dihydroxypolybutadiene (KRASOL LBH) excess.

A mixture containing 1.2% of 1,4-butanediol had a demixing temperature of about 105°C and a mixture with 0.34% was miscible at laboratory temperature. A mixture with 0.13% of glycerol was still nonmiscible at laboratory temperature (even for dilute mixtures, the cloudiness was distinct, particularly in comparison with the original KRASOL) and became miscible at about 90°C.

The miscibility limit for dipropylene glycol (at the laboratory temperature) is about 7%. In the case of 1,10-decanediol, it was found that a 1% mixture had a demixing temperature of about 90°C. The same result was obtained for the 5% mixture of 2,3-butanediol.

We tried to extract some general conclusions on the causes of polybutadiene miscibility or nonmiscibility using the ideas of two approaches formerly applied to solubility studies. The first one was based on the solvation equation developed by Abraham^{12–14}; the second one was inspired by Politzer's work in an electrostatic potential.^{15–17}

Abraham's method is described in detail in various articles and only the main results are presented here. The central equation, the solvation equation, is written^{12–14}

$$\log P = c + rR + s\pi^H + a\alpha^H + b\beta^H + l \log L^{16}$$

P is some property connected with the solubility or interactions, for instance, the partition coefficient or retention volume, descriptors R , π^H , α^H , β^H , and $\log L^{16}$ characterize the interaction capabilities of the known component (solvent), and coefficients c , r , s , a , b , and l characterize the tested compound (solute).

The solvation equation was originally designed for the interpretation of chromatographic data but it is useful also in other areas related to the intermolecular interactions. Descriptor R describes π - and n -electron interactions, π^H describes dipole–dipole or dipole-induced dipole interactions; α^H is H-bond acidity and β^H is H-bond basicity, and $\log L^{16}$ serves to describe dispersion interactions. Descriptor values for a huge amount of compounds are tabulated.^{12–14}

We made use of tabulated descriptors of the second compounds, used in the miscibility experiments, for speculations about the role of interactions in the miscibility of liquid polybutadienes. In the case when good miscibility was revealed, it is expected that the interactions, which the second component is capable of, support miscibility.

As the descriptors are easily available,^{12–14} only the conclusions with the most important evidence are presented. Polybutadienes are, of course, miscible with the compounds of very similar structures and interaction capabilities (alkanes, dispersive interactions). Miscibility with dissimilar compounds is depressed by their polarity or polarizability. Probably, also, H-bond acidity of the second component lowers its miscibility

with polybutadiene, even with hydroxyl-terminated polybutadiene. An unfavorable influence of the polarity may be outweighed by the π -electron interactions and/or H-bond basicity of the second component (the latter statement is valid particularly for the hydroxyl-terminated polybutadiene). In the case of very polar molecules (for instance, alcohols), the length of the chain has a substantial effect—a small change in the chain length may result in an appreciable change of miscibility—the entropic factor is dominant.

Examples supporting this argumentation are given in what follows: All alkane descriptors except $\log L^{16}$, the descriptor of dispersion interactions, are zero. Tested alkanes were completely miscible with KRASOL LB and LBH. Both polybutadienes thus do not differ from alkanes in their dispersive interactions. As $\log L^{16}$ may also incorporate an entropic mixing effect, it seems that this is not significant in these mixtures and is predominated by the similarity of the hydrocarbon chains.

Alcohols have very similar values of the π^H , α^H , and β^H descriptors, a low value of descriptor R , which decreases with increasing chain length, and low values of the $\log L^{16}$ descriptor, increasing with the chain length. Remember that increasing chain length supports miscibility with both KRASOL LBH and LB.

Many nonmiscible compounds have an appreciable capability for dipole interactions and high H-bond acidity. Dimethylformamide with no H-bond acidity and relatively high H-bond basicity is also nonmiscible due to very strong dipole interactions (descriptor π^H has a slightly higher value than that for nonmiscible formamide). Miscibility with diethyl ether, acetone, ethyl acetate, toluene, and chloromethanes can be explained by the influence of π -electron interactions (descriptor R) and H-bond basicity (descriptor also β^H), both outweighing the possible unfavorable dipole interactions (descriptor π^H).

Electrostatic potential is a quantity which has been successfully applied in the interpretation of various properties, among them solubility.^{15–17} Certain characteristics obtained from the electrostatic potential even have direct relations to some descriptors of the solvation equation described above.^{18,19}

For our purpose, we used the ideas from the article by Murray et al.²⁰ They did not use the electrostatic potential itself, but, rather, computed several characteristics of its distribution around a molecule. Among others, the product

$\nu\sigma_{\text{tot}}^2$ is computed. Here, σ_{tot}^2 is the total variance defined by

$$\sigma_{\text{tot}}^2 = \sigma_+^2 + \sigma_-^2$$

where σ_+^2 is some average of only positive and σ_-^2 of only negative values of the overall electrostatic potential. Parameter ν is defined by

$$\nu = \sigma_+^2\sigma_-^2/(\sigma_{\text{tot}}^2)^2$$

and has a maximum (0.25) when $\sigma_+^2 = \sigma_-^2$. The closer the value of ν to 0.25, the higher the probability of a similar strength of molecular interaction through both the area of positive and the area of negative electrostatic potential.

We have found relevancy for the product $\nu\sigma_{\text{tot}}^2$ also to our work. Values of this product available from the published survey²⁰ for some of our second components are presented in Table II together with the miscibility with KRASOLs. It is seen that some critical value of the product $\nu\sigma_{\text{tot}}^2$ exists. Compounds having the value of the product lower than critical are miscible with polybutadienes. This critical value is about 30 (kcal/mol)² for KRASOL LBH. There are not enough data for estimating the critical value for KRASOL LB; it should be lower than about 28 (kcal/mol)² [even 1-hexanol is not miscible with LB and the value of the product decreases in the homologous series from 39 (kcal/mol)² for methanol to 28.9 (kcal/mol)² for 1-butanol] and higher than about 17 (kcal/mol)².

The only exception to this rule is dimethylformamide, which should be completely miscible [$\nu\sigma_{\text{tot}}^2 = 16.7$ (kcal/mol)²]. From the compounds given in the cited article²⁰ and having $\nu\sigma_{\text{tot}}^2 < 30$ (kcal/mol)², dimethylformamide has relatively high values of σ_+^2 [18.6 (kcal/mol)²] and, in particular, σ_-^2 [158.8 (kcal/mol)²], which is similar to miscible acetone [15.9 and 159.8 (kcal/mol)², respectively] and pyridine [18.5 and 212.3 (kcal/mol)², respectively]. However, in comparison with them, dimethylformamide has a higher value of the parameter ν and of the ratios σ_+^2/σ_-^2 and $\sigma_+^2/\sigma_{\text{tot}}^2$ and a lower value of the ratio $\sigma_-^2/\sigma_{\text{tot}}^2$. The same statements about the same values are valid also for aniline, that is, for the nonmiscible compound with $\nu\sigma_{\text{tot}}^2$, only slightly higher than 30 (kcal/mol)². Thus, in the case of a compound having high partial values of its electrostatic potential, that is, σ_+^2 or σ_-^2 , it is necessary to check besides the $\nu\sigma_{\text{tot}}^2$ value also the ratios of negative

Table II Miscibility with KRASOL LBH and Its Relation to the Electrostatic Potential

Compound	Miscibility with KRASOL LB	Miscibility with KRASOL LBH	$\nu\sigma_{\text{tot}}^2$ (kcal/mol) ² (From Ref. 20)
Ethanol	0	0	36.2
2-Propanol	0	+	29.7
Ethylene glycol	—	0	47.6
Formamide	0	0	62.5
Aniline	0	0	33.0
Dimethylformamide	0	0	16.7
Cyclohexane	+	+	0.5
Toluene	+	+	4.2
Diethyl ether	+	+	7.6
Acetone	+	+	14.4
Pyridine	+	+	17.1
Tetrachlormethane	+	+	2.3
1-Butanol	p	+ ^a	28.9
Octane	+ ^b	+ ^b	0.7

For explanation of symbols, see Table I and the text.

^a Not determined but due to the result for the miscibility of *n*-propanol expected.

^b Not determined but due to the results for the miscibility of other alkanes expected.

and positive values of the electrostatic potential. A high value of the positive part of the electrostatic potential, in comparison with the negative area, imposes limitations on the miscibility of this compound with polybutadienes. This conclusion supports the old "similia similibus solvuntur" because polybutadiene, due to the double-bond electrons, may be viewed as a somewhat negatively charged molecule.

CONCLUSIONS

Qualitative information on the miscibility of liquid polybutadiene and hydroxyl-terminated polybutadiene was obtained. Although some of it could be anticipated from the molecular structures, experimental verification of such predictions should not be underestimated. Moreover, relatively vague preliminary claims were precised by the experiments and new interesting facts on the miscibility behavior were revealed.

Polar molecules are not miscible with polybutadienes. Polarity may be balanced and miscibility enhanced by supporting π -electron interaction capabilities, H-bond basicity, or a sufficiently long low-polar part of a partner molecule. Other ways of improving miscibility is unsymmetrical placement of polar groups in the molecule structure.

Thus, 1,2-diols are much more miscible than are corresponding α,ω -diols. These claims are valid, in particular, for the miscibility with the hydroxyl-terminated polybutadiene.

An entropic factor sometimes plays a substantial role in the miscibility of short polar compounds with hydroxyl-terminated polybutadiene. A small change in the molecule structure may result in an appreciable change in miscibility. Interaction capabilities through the positive area of the electrostatic potential of the partner molecule, not sufficiently compensated by the negative part, lower the miscibility with polybutadienes.

There are differences between pure and hydroxyl-terminated polybutadiene in their miscibility behavior with hydroxyl-containing compounds. The presence of only two hydroxyl groups in a relatively long hydrocarbon chain thus influences properties of the molecule. Because the pure polybutadiene may be viewed as a model of the soft segment of polybutadiene-based polyurethanes, it follows that a strongly microphase-separated product is very probably formed even from the well-miscible initial mixture.

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