

Polymer Communication

# Inverse gas chromatography of liquid polybutadienes

M. Pekař\*

Brno University of Technology, Faculty of Chemistry, Purkyňova 118, 61200 Brno, Czech Republic

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## Abstract

Results of inverse gas chromatography study of liquid polybutadiene and dihydroxypolybutadiene are presented. The study was motivated by the application of polybutadiene polyols in polyurethane chemistry where miscibility problems are often encountered. The experimental results revealed marked differences in interaction behavior of polybutadiene and dihydroxypolybutadiene, particularly with relation to the polar molecules. Influence of temperature is discussed as well as relation to the previous miscibility study. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Dihydroxypolybutadiene; Intermolecular interactions; Polybutadiene

## 1. Introduction

Liquid polybutadienes, either pure or functionalized with various groups, are polymers of versatile use. Their use is based on the reactivity of double bonds or functional groups. One of the most widely used applications is in polyurethane chemistry where hydroxyl-containing polybutadienes are used as polyol components. Polybutadiene-based polyurethanes should have excellent hydrolytic resistance, low temperature properties and elasticity [1,2]. However, their mechanical properties are lower in comparison with conventional, polyether- or polyester-based materials. Low polarity of the polybutadiene backbone is often claimed to be responsible for this lowering [3]. The other components, i.e. isocyanates, chain extenders, and crosslinkers, are usually more polar and miscibility problems impair desired phase structure and restrict contact of reacting molecules.

There are a few published studies on IGC of (low molecular weight) polybutadienes [4,5] but to the best of our knowledge there is no study on hydroxyl-terminated polybutadienes. Munk et al. [4] studied poly(1,2-butadiene) of unknown molecular weight at 100°C. Alessi et al. [5] studied three polybutadienes of various microstructure and the following molecular weights ( $M_n$ ): 11900, 11800, 88000, at 40, 60, 80 and 100°C.

Recently, new types of liquid polybutadienes, prepared by anionic polymerization, were introduced by the Kaučuk company under the trade name Krasol [6]. In order to

optimize properties of Krasol-based polyurethanes and fully understand the role of miscibility, an extensive study of Krasols phase behavior has been initiated. This communication reports on the first results obtained from inverse gas chromatography (IGC). IGC was used to obtain insights into the intermolecular interaction capabilities of liquid polybutadienes, which underlie their phase behavior. Moreover, as Krasol is produced both in unfunctionalized and hydroxyl-terminated form, the effect of two hydroxyl groups in relatively long hydrocarbon chain can be evaluated.

## 2. Experimental

Two liquid polybutadienes were used with the following producer specifications.

Krasol LB — unfunctionalized liquid polybutadiene,  $M_n = 2225$ ,  $M_w = 2608$ ; Brookfield viscosity 8 Pas (25°C).

Krasol LBH — hydroxyl terminated polybutadiene,  $M_w = 2610$ ,  $M_n = 2310$ ; OH-content 0.765 mmol/g;  $f_2 = 91.4\%$ ,  $f_1 = 7.5\%$ ,  $f_0 = 1.1\%$  (fractions of bi-, mono-, and non-functional chains, respectively); Brookfield viscosity 16 Pas (25°C).

Krasols contain 60% of 1,2-(vinyl) unit, 25% of 1,4-*trans* and 15% of 1,4-*cis* structural units.

Densities of polybutadienes were kindly measured by Mettler–Toledo company using their vibrational densitometer with the following results at 40 and 60°C, respectively: LB — 879.0 and 867.0 kg/m<sup>3</sup>, LBH — 887.9 and 875.9 kg/m<sup>3</sup>.

Solvents and solutes for IGC from various sources were

\* Fax: +420-5-412-1697.

E-mail address: pekar@fch.vutbr.cz (M. Pekař).

Table 1  
Specific retention volumes ( $V_g$ ) on Krasols LB and LBH and interaction parameters ( $\chi$ ) at 40°C (top) and 60°C (bottom)

Solute	$V_g$ (dm <sup>3</sup> /g)		$\chi$	
	LB	LBH	LB	LBH
Isopropylalcohol	0.0557	0.1016	2.899	2.287
	0.0276	0.0481	2.644	2.078
<i>n</i> -propylalcohol	0.1045	0.2111	2.979	2.266
	0.0486	0.0906	2.741	2.108
<i>n</i> -butylalcohol	0.2762	0.6187	2.843	2.027
	0.1216	0.2280	2.548	1.909
Isobutylalcohol	0.1807	0.3800	2.774	2.020
	0.0828	0.1513	2.482	1.869
<i>t</i> -butylalcohol	0.0639	0.1277	2.561	1.858
	0.0342	0.0573	2.215	1.689
<i>n</i> -pentylalcohol	0.7050	1.7597	2.780	1.855
	0.1985	0.5673	2.821	1.761
<i>n</i> -hexylalcohol	1.9438	4.6970	2.642	1.750
	0.7165	1.3924	2.322	1.647
Benzene	0.3156	0.2682	0.454	0.607
	0.1481	0.1489	0.509	0.493
Nitromethane	0.0909	0.1095	3.113	2.917
	0.0475	0.0882	2.956	2.327
Pyridine	0.7772	1.1040	1.056	0.694
	0.3229	0.4257	1.086	0.799
Methylacetate	0.0686	0.0812	1.311	1.132
	0.0352	0.0392	1.307	1.189
Ethylacetate	0.1479	0.1781	1.920	0.896
	0.0704	0.0796	1.094	0.961
<i>n</i> -butylacetate	0.9362	1.2713	0.961	0.644
	0.4083	0.4554	0.859	0.739
<i>n</i> -pentylacetate	2.5581	1.7088	0.803	1.196
	0.9895	1.1048	0.732	0.611
Cyclohexane	0.2497	0.2219	0.485	0.593
	0.1216	0.1229	0.519	0.498
<i>n</i> -pentane	0.0415	0.0361	0.700	0.829
	0.0231	0.0210	0.735	0.820
<i>n</i> -hexane	0.1099	0.0922	0.709	0.874
	0.0545	0.0496	0.755	0.839
<i>n</i> -heptane	0.3010	0.2448	0.682	0.879
	0.1326	0.1197	0.739	0.832
<i>n</i> -octane	0.8267	0.6560	0.653	0.875
	0.3241	0.2892	0.719	0.822
<i>n</i> -nonane	2.2606	1.7485	0.623	0.870
	0.7860	0.6965	0.703	0.814

all of analytical purity grade. Solutes modeling various polarity effects or containing functional groups with relation to the polyurethane applications of polybutadienes were used.

Gas chromatograph CHROM 5 (Laboratorní Přístroje, Czech Republic) with an FID detector was used, with nitrogen as a carrier gas. A glass column (3 × 2500 mm) was filled with CHROMATON NAW kieselguhr (0.125–0.160 mm particle size; Lachema, Czech Republic) coated by polybutadiene. Standard impregnation procedure from acetone solution was used. The deposited amount of polybutadiene was determined using Soxhlet extraction with acetone. The amounts of Krasol LB and Krasol LBH (by weight) were 9.6 and 9.7%, respectively.

Dead retention time was determined using a standard

C<sub>5</sub>–C<sub>9</sub> alkanes kit (Polyscience 211CX). Chromatographic measurements were made at 40 and 60°C. At higher temperatures the polybutadiene coating was not stable.

Specific retention volumes were determined as:

$$V_g = F(t_r - t_m)j/m$$

where  $F$  is the carrier gas flow measured by bubble flowmeter, pressure and temperature corrected [5],  $t_r$  is the retention time of the solute,  $t_m$  is the dead retention time,  $j$  is the compressibility correction factor and  $m$  the polybutadiene weight on the column. Factor  $j$  is given by:

$$j = (3/2)[(p_i/p_o)^2 - 1]/[(p_i/p_o)^3 - 1]$$

where  $p_i$  and  $p_o$  is pressure at column inlet and outlet respectively.

### 3. Results and discussion

Results are presented in Table 1 as specific retention volumes and Flory–Huggins interaction coefficient obtained as [4]:

$$\chi = \ln(RT\nu_p/V_g p_s^o V_s) - 1 + V_s/M_p \nu_p - (B_s - V_s)p_s^o/RT$$

where  $\nu_p$  is polybutadiene specific volume,  $V_g$  is specific retention volume,  $p_s^o$  is solute vapor pressure,  $V_s$  is its molar volume,  $M_p$  is polybutadiene molecular weight and  $B_s$  is solute second virial coefficient. Data for solutes were taken from Refs. [7–10]. Specific retention volume and solute vapor pressure have the greatest influence on the value of interaction coefficient.

There are marked differences in the retention characteristics of the solutes containing polar group on polybutadiene (Krasol LB) and dihydroxypolybutadiene (Krasol LBH) which are reflected in differences in interaction coefficients. On the other hand, retention parameters of alkanes differ only slightly, particularly at lower temperature and shorter alkanes. Interaction coefficients of alkanes on Krasol LBH are higher than on LB. Thus, presence of only two hydroxyl groups in relatively long hydrocarbon chains (average polymerization degree of Krasols was about 50) can substantially affect its intermolecular interactions and, consequently, miscibility. Retention trends within homological series, e.g. alcohols, acetates, or alkanes, are yet retained.

As expected, the longer the linear chain of aliphatic alcohols the higher their specific retention volume on both types of liquid polybutadiene and the lower the interaction coefficient, because of the predominating effect of the non-polar part of the molecule. Similar argumentation can be used to explain the retention behavior of acetates. Branched C<sub>4</sub> alcohols have lower retention volumes but also lower interaction coefficients than linear isomers. This is probably caused by steric reasons and consequential physical properties (particularly, vapor pressure). Isopropylalcohol has a retention of about 50% lower than *n*-propyl alcohol for

both polybutadienes but their interaction coefficients are much closer, particularly due to the difference in vapor pressures, again.

Retention differences between polybutadiene and dihydroxypolybutadiene should be attributed mainly to the influence of hydrogen bonding of hydroxyl groups. Thus, specific retention volumes of alcohols or acetates are higher and interaction coefficients lower on Krasol LBH. Elevated temperatures reduce this difference to a certain degree. Therefore, there is a moderate temperature effect on the hydrogen bonding.

Specific retention volumes of alkanes are higher on Krasol LB and become higher as the alkane molecule gets longer; interaction coefficients are higher on LBH. This can be viewed as the adverse effect of hydroxyl groups on Krasol LBH increasing its polarity. The difference is more pronounced at the lower temperature, i.e. elevated temperatures restrain the unfavorable effect of Krasol LBH polarity on alkane retention. Whereas alkanes interaction coefficients on Krasol LB are decreasing in homological series and slightly increasing with temperature, on LBH they are much closer and slightly decreasing with temperature. Changes in retention volumes of alkanes on Krasol LBH, due to repulsive effect of hydroxyl groups, are more compensated by changes in vapor pressures of alkanes.

Lower specific retention volume of benzene on Krasol LBH at 40°C is probably due to the higher polarity of dihydroxypolybutadiene. At 60°C this effect is repressed and the retention volumes are almost equal.

Pyridine, possessing higher polarity and proton-acceptor function in the hydrogen bond, has higher specific retention volume and lower interaction coefficient on Krasol LBH at both temperatures. Increased temperature reduces the difference only slightly.

Nitromethane can be viewed as a highly polar substance. Its specific retention volume and interaction coefficient at 40°C are comparable for both polybutadiene types. However, at 60°C the specific retention volume on Krasol LBH is almost two-fold and interaction coefficient is about 20% lower. In this case, temperature probably supports the effect of nitromethane polarity and the decrease of specific retention volume with temperature is more considerable for Krasol LB than LBH. Temperature thus has the opposite influence on the polarity of nitromethane than of Krasol LBH.

Results of IGC experiments nicely accord with findings of our qualitative study on the miscibility behavior of liquid polybutadienes Krasol [11]. This study found marked differences in miscibility of Krasols LB and LBH with hydroxyl compounds, presented the influence of chain length of 1-alkanols on the phase diagram of their mixture with Krasol LB, which can be briefly described as reducing the critical temperature with increasing chain length. Results of the miscibility study led also to speculations about the

substantial role of hydrogen bonding in the miscibility behavior of Krasol LBH.

Comparison of our and published results is not straightforward. The other studies [4,5] used polybutadienes with different molecular weights, no functionalized polybutadienes, and Munk et al. [4] give results only for 100°C. Published specific retention volumes and their trends within homologous series are comparable with the results obtained in our work. Also, relative trends in values of interaction parameters are comparable, the values themselves are usually somewhat higher on Krasol LB than on polybutadienes used in the published studies. Alessi et al. [5] also found similar non-unidirectional trends in temperature dependence of interaction coefficients for some solutes.

#### 4. Conclusions

Inverse gas chromatography revealed marked differences in the retention behavior of polybutadiene and dihydroxypolybutadiene, particularly to the solutes containing polar groups. The presence of only two hydroxyl groups in a relatively long hydrocarbon chain can substantially affect its intermolecular interactions and, consequently, miscibility. Introducing hydroxyl groups support miscibility of polybutadiene with more polar substances while leaving the miscibility with non-polar molecules almost unchanged.

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