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Effect of polymer microstructure on solubility characteristics and interactions

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Abstract: The effect of polymer microstructure on the solubility characteristics and propensity for interactions of polybutadiene (PBD) has been studied by means of the general solvation equation using data reported by Alessi et al. An increase in the vinyl content from 8% to 69% did not affect the propensity of PBD to interact with π and n electron pairs and with dipolar – polarisable probes. In contrast, the hydrogen-bond basicity decreased due to steric hindrance from the alkene side group.

Key words: Polybutadiene – microstructure – solubility – interactions – solvation constants – hydrogen bond acidity – hydrogen bond basicity

Introduction

The effect of polymer microstructure on the physical and mechanical properties of polymers is well established [1]. For instance, polybutadiene containing in excess of 80% cis 1,4-units crystallises on stretching while cis-contents of 25 to 80% lead to an amorphous material [2, 3]. In contrast, the effect of microstructure on the propensity of the polymer to interact and its solubility characteristics is not well established because of the lack of appropriate parameters. The conventional solubility parameters are not sufficiently sensitive to deconvolute such effects. The three-dimensional solubility parameters can perhaps offer an alternative approach but the parameters themselves are arbitrary and very difficult to determine experimentally.

Alessi et al. [4] have recently determined specific retention volumes, V_g, for 35 probes on three polybutadienes with varying molecular weight and microstructure at different temperatures. The purpose of this paper is to show that from the experimental values of V_g and using the general solvation equation, a considerable amount of information can be obtained on the effect of polymer microstructure on the solubility characteristics and interaction propensity of polybutadiene.

Solvation constants

We have already shown [5, 6] that V_g or L values for a series of probes on a given polymeric phase can be correlated, as Log V_g or Log L, through the general solvation equation.

$$\text{Log}\, V_g = c + r\, R_o + s\, \pi_o^H + a\, \alpha_o^H + b\, \beta_o^H + 1\, \text{Log}\, L_o^{16}\,. \qquad (1)$$

Subscript o denotes the probes. Note that V_g is the retention volume at the column temperature and L is the Ostwald solubility coefficient, L. The two parameters are interrelated through the density of the stationary phase at the column temperature, d_T:

$$L = V_g d_T \qquad (2)$$

The explanatory variables are probe properties. R_o is the excess molar refraction, π_o^H is the dipolarity/polarisability, α_o^H and β_o^H are the probe hydrogen-bond acidity and basicity, and L_o^{16} is the Ostwald solubility coefficient of the solute probe on hexadecane at 298 K. The characteristic constants of Eq. (1), *c*, *r*, *s*, *a*, *b* and 1, describe quantitatively the solubility-related properties of a polymer. The constant r indicates the propensity of the polymer to interact with π and n electron pairs and is usually slightly positive, except in fluorinated polymers. The s constant relates to the interaction of the polymer with dipolar-polarizable probes, the a constant to the polymer hydrogen-bond basicity (because acidic probes will interact with the basic polymer) and the b constant to the hydrogen-bond acidity. The 1 Log L_0^{16} term is a composite of endoergic cavity formation and exoergic general dispersion interactions. The latter always dominates, leading to a positive 1 value. Similarly the exoergic interactions described by the $s\pi_0^H$, $a\alpha_0^H$ and $b\beta_0^H$ terms must always lead to positive *s*, *a* and *b* constants. The constants of Eq. (1) are determined by multiple linear regression analysis. All values of the probe explanatory variables are from a previous compilation [7].

Table 1. Molecular weight and microstructure of the polybutadienes (PBD1, PBD2, PBD3, PBD4)

		% of isomer		
Polymer	$\bar{M}_W$	1,4-trans	1,4-cis	1,2-
PBD 1	12200	45.5	46.5	8.0
PBD 2	13000	10.2	20.8	69.0
PBD 3	108000	46.5	40.6	12.9
PBD 4	24000	52.0	40.0	8.0

Table 2. The probes used by Alessi et al. [4] and their solvation parameters. Only probes marked with * were used for PBD3

PROBE	*No.*	*R*	*s*	*a*	*b*	1 Log *L* 16
n pentane	106	0.000	0.000	0.000	0.000	2.162
n hexane	109	0.000	0.000	0.000	0.000	2.668
n heptane*	114	0.000	0.000	0.000	0.000	3.173
n octane*	126	0.000	0.000	0.000	0.000	3.677
hex-1-ene	1015	0.078	0.080	0.000	0.070	2.572
hept-1-ene	1030	0.092	0.080	0.000	0.070	3.063
oct-1-ene*	1040	0.094	0.080	0.000	0.070	3.568
cyclohexane*	701	0.305	0.100	0.000	0.000	2.964
methylcyclohexane	702	0.244	0.100	0.000	0.000	3.323
ethylcyclohexane	710	0.263	0.100	0.000	0.000	3.877
benzene*	10001	0.610	0.520	0.000	0.140	2.786
toluene*	10002	0.601	0.520	0.000	0.140	3.325
acetone	5501	0.179	0.700	0.040	0.490	1.696
butan-2-one*	5502	0.166	0.700	0.000	0.510	2.287
MiBK*	5509	0.111	0.650	0.000	0.510	3.089
DEK*	5504	0.154	0.660	0.000	0.510	2.811
methanol	8001	0.278	0.440	0.430	0.470	0.970
ethanol	8002	0.246	0.420	0.370	0.480	1.485
propan-1-ol*	8003	0.236	0.420	0.370	0.480	2.031
propan-2-ol	8004	0.212	0.360	0.330	0.560	1.764
butan-1-ol*	8005	0.224	0.224	0.420	0.480	2.601
acetonitrile	6601	0.237	0.900	0.070	0.320	1.739
propionitrile*	6602	0.162	0.900	0.020	0.360	2.082
methyl acetate	6051	0.142	0.640	0.000	0.450	1.911
ethyl acetate*	6052	0.106	0.620	0.000	0.450	2.314
propyl acetate*	6053	0.092	0.600	0.000	0.450	2.819
butyl acetate	6055	0.071	0.600	0.000	0.450	3.353
chloroform*	2503	0.425	0.490	0.150	0.150	2.480
carbon tetrachloride*	2504	0.458	0.380	0.000	0.000	2.823
1 chloropropane*	2514	0.216	0.400	0.000	0.100	2.202
1 chlorobutane*	2530	0.210	0.400	0.000	0.100	2.722
1 chloropentane	2550	0.208	0.400	0.000	0.100	3.223
tetrahydrofuran	5110	0.289	0.520	0.000	0.480	2.636
diethyl ether	4502	0.041	0.250	0.000	0.450	2.015
dipropyl ether	4503	0.008	0.250	0.000	0.450	2.954

Results and discussion

The three polybutadienes were prepared by anionic polymerisation with tert-butyl lithium as initiator and terminated with dry 2-propanol [4]. The polymers were precipitated from the cyclohexane solution with methanol and dried under vacuum. The polymer molecular weight was controlled by the concentration of initiator. The 1,2-content in the polymer was controlled by changing the polarity of the cyclohexane solvent by addition of tetra-hydrofuran for PBD1 and PBD2 (Table 1).

The first application of the full equation 1 was to the full set of probes (Table 2) available on each polymer. V_g values for the full set of 35 probers were available for PBD1 and PBD2; Data for only 18 probes were available for PBD3. In all three cases, the *b* constant was negative and the correlation coefficient was unacceptably small. Consequently the corresponding term, $b\beta_o^H$, was eliminated from Eq. (1). This suggests that all three polybutadiene polymers do not possess any hydrogen-bond acidity, in agreement with earlier analysis [8]. Increasing temperature decreases the characteristic constants for the exoergic interactions described by the hydrogen-bond basicity and the dipolarity–polarisability terms. A similar effect was observed for the term describing the propensity of the polymer to interact with π and n electron pairs.

Table 3 summarises the characteristic constants for the three PBD grades together with values reported earlier [8]. The characteristic constants were calculated using the full set of 35 probes for PBD1 and PBD2, and the set of 18 probes for PBD3. Comparison of the characteristic constants (Table 3) of PBD1 and PBD2 shows that increasing the vinyl content in the polymer microstructure from 8% to 69% does not have a significant effect on the *r*, *s* and 1 constants. This suggests that there is no effect on the propensity of the polymer to interact with the π and n electron pairs and with dipolar-polarisable probes. The hydrogen-bond basicity of the polymer as measured by the a-constant, though, decreased, indicating that the 1,2-content in the polybutadiene chain influences the propensity of the polymer to participate in hydrogen-bond interactions as a hydrogen acceptor, perhaps due to steric hindrance from the alkene side group. This would have significant implications in the compatibility and, hence morphology, in blends of polybutadienes with other polymers capable of acting as hydrogen-bond acids such as phenolic resins. PBD3, on the other hand, with microstructure comparable to that of PBD1 but with higher molecular weight, showed significantly higher hydrogen-bond basicity and dipolarity–polarisability characteristic constants but comparable excess molar refraction and cavity terms. The former is consistent with less steric hindrance

Table 3 Characteristic constants for the polybutadiene grades (see Table 1)

T/ °C	R	π_2^H	α^{2H}	Log L^{16}	c	r	F	n
PBD 1								
100	0.245	0.330	0.372	0.620	− 0.265	0.9979	1525	31
80	0.212	0.381	0.444	0.693	− 0.254	0.9979	1554	32
60	0.158	0.454	0.488	0.758	− 0.190	0.9974	1239	31
PBD 2								
100	0.165	0.336	0.278	0.625	− 0.189	0.9981	1612	30
80	0.119	0.391	0.314	0.694	− 0.164	0.9982	1787	31
60	0.067	0.447	0.337	0.769	− 0.126	0.9980	1543	30
40	0.043	0.504	0.433	0.849	− 0.077	0.9967	1005	32
PBD 3								
100	0.152	0.541	0.726	0.596	− 0.243	0.9980	829	18
80	0.113	0.598	0.964	0.664	− 0.223	0.9976	666	18
60	0.070	0.660	1.230	0.738	− 0.193	0.9960	403	18
PBD 4								
100	0.133	0.355	0.201	0.623	− 0.275	0.9992		43

Table 4. Solvation constants for the three PBD grades at 373K for the set of 18 probes used for PBD3

Polymer	$r\,R$	$s\,\pi_2^H$	$a\,\alpha_{2H}$	l Log L^{16}	r	F
PBD1†	0.251	0.304	0.283	0.614	0.9970	500
PBD2††	0.103	0.306	0.212	0.619	0.9952	398
PBD3	0.152	0.541	0.726	0.596	0.9980	829

PBD1†: Set of 18 probes excluding DEK
PBD2††: Set of 18 probes excluding hept-1-ene

due to the lower amount of the side alkene groups. The significantly higher hydrogen-bond basicity characteristic constant for PBD3 compared to PBD1 is not quite clear at present. Earlier work with polyethylene oxide [9] has shown that the hydrogen-bond basicity is sensitive to polymer molecular weight up to molecular weights of 3000, thereafter levelling off. We have attributed this effect to the number of terminal hydroxyls. In the case of polybutadiene, any increase in the molecular weight would result in a decrease in the number of tert-butyl and methyl groups. In order to make sure that the differences in the characteristic constants between PBD1 and PBD3 were not due to the significantly different number of probes used in the regression analysis, we repeated the regressions with the set of 18 probes used for PBD3 (Table 4). Although the reduction in the number of probes has a significant effect in the characteristic constants as expected, the relative trend between PBD1 and PBD3 remained the same. This would suggest that the differences in the characteristic constants shown in Tables 3 and 4, were not fundamentally due to changes in the number of probes.

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