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The Study of Modified Poly(Styrene-co-Divinylbenzene) by Inverse Gaschromatographic Analysis

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SUMMARY:

For modified poly(styrene-co-divinylbenzene) the changes in supermolecular structure resulting from diluting the monomers during copolymerization with various amounts of inert diluents were studied. It has been found that the copolymers, obtained in the presence of substantial amounts of diluent, have a looser structure than those obtained with less diluent, as suggested by both the swelling measurements and the results of the inverse gas chromatographic (IGC) analysis. By this latter method it was found that the looser the copolymer structure, the broader was the range of adsorption-absorption nonequilibrium region and the lower was the heat of adsorption of normal aliphatic alcohols by the copolymers. Since the copolymers had the same crosslinking degree, no difference in their apparent glass transition temperatures were detected.

ZUSAMMENFASSUNG:

Die durch Lösen der Monomeren in verschiedenen Anteilen inerter Lösungsmittel während der Copolymerisation hervorgerufenen Änderungen der übermolekularen Struktur wurden für modifizierte Styrol/Divinylbenzolcopolymere untersucht. Durch Quellungsmessungen und Anwendung der inversen Gaschromatographie wurde nachgewiesen, daß Copolymere, die in Anwesenheit größerer Lösungsmittelmengen hergestellt wurden, eine lockerere Struktur besitzen als diejenigen, deren Polymerisation in geringen Lösungsmittelmengen durchgeführt wurde. Durch die inverse Gaschromatographie ergab sich, daß die Breite der Adsorptions-Absorptions-Nichtgleichgewichtsregion zunahm, je lockerer der Polymeraufbau war. Gleichzeitig nahm die Adsorptionswärme für aliphatische Alkohole ab. Da die Copolymeren den gleichen Vernetzungsgrad aufwiesen, wurden keine Unterschiede der Glasübergangstemperatur beobachtet.

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Introduction

The supermolecular structure of crosslinked vinyl polymers significantly changes when monomers polymerize in the presence of varying amounts of inert diluents. While studying poly(styrene-co-divinylbenzene) (S-DVB) polymers of high degree of crosslinking, it has been shown that the gel formed in the presence of high amounts of diluent is highly heterogeneous[1]: portions of highly crosslinked polymer were formed interconnected with relatively loose reticulated parts. In the condensed state, the structure of these polymers was cauliflower-like[2]. The chain fragments in the loosely crosslinked portions exhibited relatively high mobility. Indeed, the penetration moduli measured for the inhomogeneous S-DVB copolymers were found to decrease as the degree of dilution of monomers used for their preparation increased[3].

The mobility of polymer segments can be measured indirectly using the inverse gas chromatography (IGC) technique. In a recent paper[4], the effect of the overall crosslinking density (amount of DVB) on the apparent glass transition temperature of diluent modified S-DVB copolymers was reported. It has been found that the exact T_g values, i. e., the same as those obtained by DSC, can be obtained by IGC while using n-propanol or n-butanol as molecular probes. From the retention diagrams obtained by IGC, it was possible to calculate isosteric heats of adsorption of aliphatic alcohols onto S-DVB copolymers. These values were the smallest for butanol[4].

For the system S-DVB copolymers/aliphatic alcohols, the adsorption-absorption equilibrium could be reached at the temperature exceeding T_g by ca. 50 K; the absorption part of the retention diagrams was also recorded and the thermodynamic parameters of the system[5], including Hildebrand solubility parameters of S-DVB copolymers, were calculated. The latter had the same value as those evaluated by other methods[6].

In the present work, the effect of dilution of S-DVB mixtures during copolymerization on the supermolecular structure of the obtained copolymers was investigated. The chromatographic columns were filled with the copolymers and the retention diagrams were evaluated for straight chain aliphatic alcohols $C_1 - C_6$. The applied procedure was exactly the same as that described elsewhere[4].

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Results and Discussion

The copolymers were obtained by suspension copolymerization of styrene and commercial divinylbenzene carried out in the presence of varying amounts of heptane (H)/toluene (T) mixture (1:9 by volume). The numbers 0.5, 0.4, and 0.3 appearing between HT 19 and /10 in the copolymer codes (Tab. 4) denote the volume fraction of the monomers in the copolymerization system. The nominal crosslinking degree was 10 wt.-% of DVB[4].

The copolymers obtained under these conditions were non-porous (Tab. 1). Their swelling degree, however, as expressed in terms of toluene regain (W) increases with the dilution of monomers. The increasing toluene

Tab. 1. Characteristics of S/DVB copolymers.

Property	Solvent	HT 19 × /10[a]		
		0.5[a]	0.4[a]	0.3[a]
Porosity		0.05	0.05	0.05
W	Toluene	1.8	1.92	2.46
V_2		0.32	0.30	0.25
Q		2.9	2.8	2.6
W	Methanol	0.18	0.19	0.19
V_2		0.81	0.79	0.79
Q		9.6	8.8	8.7
W	n-Propanol	0.23	0.26	0.23
V_2		0.78	0.75	0.76
Q		8.4	7.4	7.7
W	n-Hexanol	0.22	0.23	0.22
V_2		0.78	0.78	0.79
Q		8.4	8.4	8.7
W	Water	0.05	0.06	0.07
V_2		0.96	0.94	0.93
Q		45.6	30.1	25.8

W : solvent regain g/g
V_2 : volume fraction of the polymer in swollen copolymer
Q : Prager tortuosity factor
a : volume fraction of the monomers (S/DVB)

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regain indicates that the structure of the copolymers, obtained in better solvating conditions, is looser.
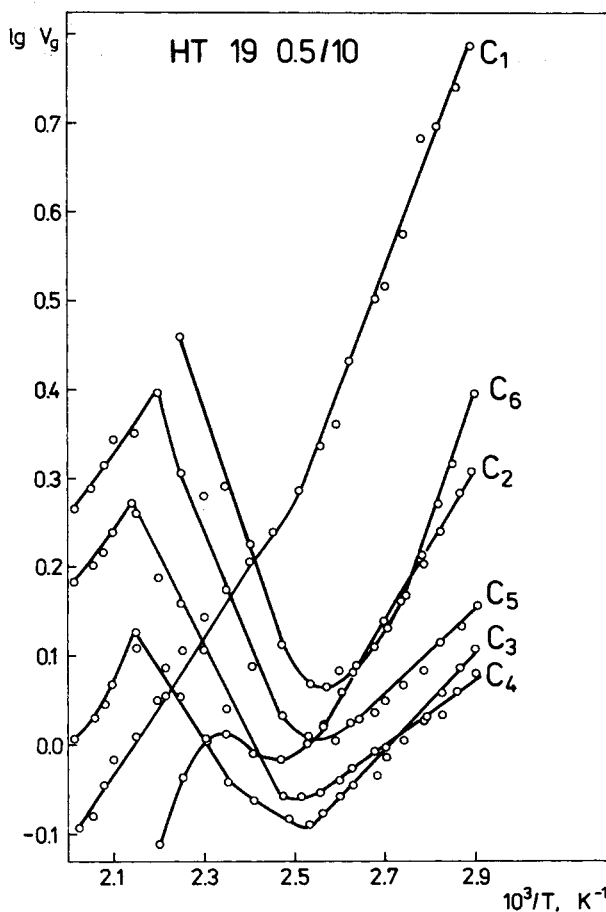

Fig. 1. Retention diagrams of normal aliphatic alcohols $C_1 - C_6$ on S-DVB copolymer HT 19 0.5/10.

The regains of alcohols increases with increasing molar mass of the alcohols, since the higher the molecular mass of an alcohol, the better solvent it becomes. On the other hand, the diffusion of alcohols within gels is reduced as their molecular size increases. This effect is clearly seen in the
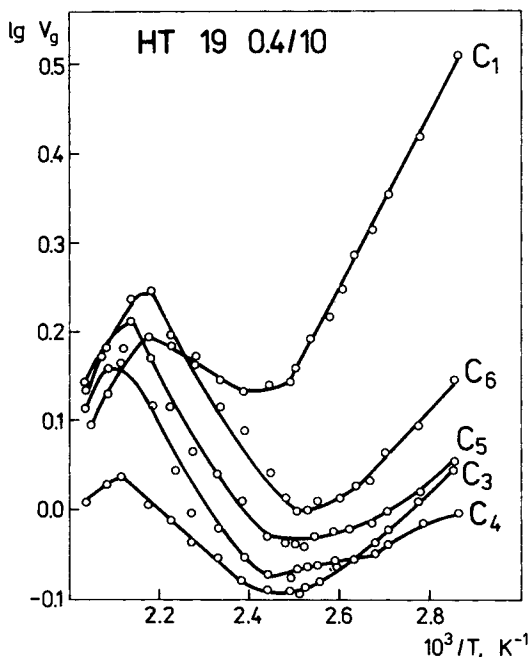
Fig. 2. Retention diagrams of normal aliphatic alcohols on S-DVB copolymer HT 19 0.4/10.

case of n-propanol for which the swelling degree is the highest (the lowest V_2 value), although higher alcohols are thermodynamically better solvents with respect to polystyrene. Another parameter illustrating the ability of solvents to diffuse into copolymer gels is the tortuosity factor of Prager[7]. As can be seen in Tab. 1, the tortuosity factors for the copolymer 0.5 are the highest. Thus, the copolymers obtained with a larger amount of diluent (among which the good solvent, toluene, consists 90 vol.-%) has the most expanded structure[3].

The retention diagrams for all alcohols on the copolymers 0.5, 0.4, and 0.3 are similar with slightly smaller retention volumes and slopes of lines in the adsorption regions for the copolymers 0.4 and 0.3 than those for the 0.5 copolymer (Fig. 1 – 3). The analysis of the adsorption regions shows that there are significant differences in the relationships recorded for methanol and ethanol. The plot log V_g vs. $1/T$ for methanol and copolymer 0.5 is

linear in almost the whole temperature range (Fig. 1), and it is similar to those recorded for the systems Synachrom ES-methanol[8] and polystyrene-hexadecane[9] with a thin layer of the polymer on a support. In the retention diagrams recorded for other alcohols, a large non-equilibrium region can be observed. Such a shape of retention diagrams can be related to the higher permeability of gel for the 0.4 and 0.5 copolymers where the adsorption-absorption equilibrium cannot be reached in a large temperature range (Fig. 1 – 3).
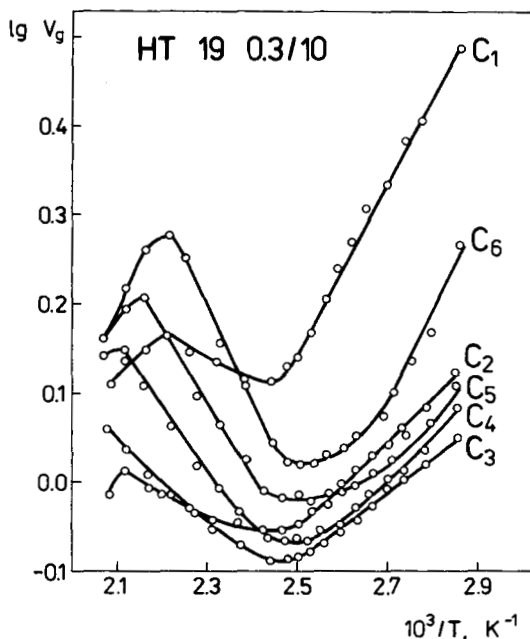

Fig. 3. Retention diagrams of normal aliphatic alcohols on S-DVB copolymer HT 19 0.3/10.

The lowest retention volumes were recorded for n-propanol. The T_g value of copolymer 0.5 read out from the diagram obtained for n-butanol is the closest to the value, determined directly by DSC (Tab. 2). The latter method gives 116 °C[10].

The values of the apparent T_g values, as read out from the retention diagrams to be the first significant deviation of a point from the straight line

Tab. 2. Apparent glass transition temperatures (T_g) of S/DVB copolymers as measured by IGC, using normal aliphatic alcohols $C_1 - C_6$ as molecular probes.

Alcohols	HT 19 × / 10		
	0.5	0.4	0.3
C_1 Methanol	125	129	130
C_2 Ethanol	123	123	130
C_3 n-Propanol	121	121	127
C_4 n-Butanol	116	115	115
C_5 n-Pentanol	105	110	109
C_6 n-Hexanol	96	111	110
DSC[10]	116	—	—

obtained in the adsorption region, are listed in Tab. 2 and 3. The highest apparent T_g values are determined for methanol and ethanol, for n-propanol and n-butanol they are close to those determined by DSC[10], and they are too small for n-pentanol and n-hexanol. The plastification and antiplastification phenomenon was already observed, and there still exists a controversy on what solvents should be used for determining T_g[11]. This problem with respect to S-DVB copolymers has been discussed elsewhere[4]. For highly crosslinked copolymers care must be taken while reading out a T_g value from retention diagrams. The best results give the correlation analysis. Otherwise, only approximate values may be obtained[8].

The slopes of the regression lines provide also the values of isosteric heats of adsorption (q_{iz}). For the studied copolymers these heats decrease from C_1 to C_4 and increase again according to increasing strength of polymer-solvent interactions (Tab. 4). The initial drop in the heat of adsorption with increasing length of the aliphatic chain of alcohols is quite different to those observed for Poropak Q[12] and for graphitized carbon black. The relationship between q_{iz} and the number of carbon atoms in the aliphatic chain of alcohols (Tab. 4) is similar to that observed for S-DVB copolymers differing in crosslinking degree[4], and it is probably related to the solubility of sorbates, particularly alcohols C_3 and C_4, in copolymers. For higher alcohols the size of sorbate molecules seems to have an effect.

Tab. 3.   The results of regression analysis of the adsorption region in the retention diagrams.

HT 19 0.5/10

Regression equation	1360×-3.15	836.7×-2.12	518.8×-1.52	402.6×-0.91	540.0×-1.41	148×-3.1
Correlation coefficient	0.9996	0.9990	0.9942	0.9976	0.9967	0.9949
Standard deviation	0.0047	0.0044	0.0069	0.0027	0.0033	0.0091
Number of points	11	10	11	8	7	5
Confidence interval						
$0.95 \pm$	0.010	0.010	0.015	0.006	0.008	0.024
$0.99 \pm$	0.015	0.014	0.022	0.009	0.012	0.037

HT 19 0.4/10

Regression equation	974.3×-2.28	392.7×-1.03	432.5×-1.19	214.12×-0.62	369.7×-1.42	544.6×-1.44
Correlation coefficient	0.9993	0.9986	0.9907	0.9968	0.9995	0.9982
Standard deviation	0.0043	0.0024	0.0026	0.0018	0.0011	0.0031
Number of points	9	8	8	7	5	5
Confidence interval						
$0.95 \pm$	0.010	0.0055	0.006	0.004	0.003	0.008
$0.99 \pm$	0.014	0.008	0.009	0.006	0.005	0.012

HT 19 0.3/10

Regression equation	950×-2.84	466.4×-1.22	406.9×-1.10	434.6×-1.17	555.1×-1.47	963.1×-2.49
Correlation coefficient	0.9996	0.9970	0.9966	0.9946	0.9991	0.9953
Standard deviation	0.0024	0.0262	0.0018	0.0011	0.0031	
Number of points	10	10	9	9	6	6
Confidence interval						
$0.95 \pm$	0.007	0.009	0.008	0.011	0.005	0.020
$0.99 \pm$	0.010	0.013	0.011	0.015	0.008	0.030

Tab. 4. Isoteric heats of adsorption (q_{iz}) of normal aliphatic alcohols on S/DVB copolymers (HT 19 ×/10).

Alcohol	δ_1 (MPa$^{1/2}$)	$\delta_1 - \delta_2$ (MPa$^{1/2}$)	q_{iz} (KJ/mol)		
			0.5	0.4	0.3
C_1 Methanol	29.7	11.1	14.3	11.5	11.2
C_2 Ethanol	26.0	7.4	10.3	6.6	7.2
C_3 n-Propanol	24.3	5.7	7.9	7.0	6.7
C_4 n-Butanol	23.3	4.7	6.7	5.2	7.2
C_5 n-Pentanol	22.3	3.7	7.2	6.2	7.7
C_6 n-Hexanol	21.9	3.3	13	7.6	11.1

δ_2 = 18.6 MPa$^{1/2}$

From the absorption region of retention diagrams (starting at ca. 50 K above T_g) a number of thermodynamic parameters for the system polymer-solvent can be calculated[13,14]. For the copolymer HT 19 0.5/10 such parameters were reported previously[5,6]. For the copolymers obtained with more diluent (0.4 and 0.3) the nonequilibrium region was found to be broader than for copolymer 0.5 and due to limited thermal stability of the samples similar information on polymer-solvent interaction could not be evaluated. Besides, such information would be of little value with respect to the super-molecular structure, since above T_g it is expected to change anyway.

Conclusions

The hypothesis concerning high heterogeneity of S-DVB copolymers obtained with large amounts of inert diluents has been confirmed by IGC method. This heterogeneity brings about a high temperature of establishing the adsorption-absorption equilibrium and nonlinear relationship between the isosteric heat of adsorption and the number of carbon atoms in the chains of aliphatic alcohols used as molecular probes. This nonlinearity is related to better penetration of n-propanol and n-butanol to copolymer gel. The copolymers obtained with the highest amounts of inert solvents have lower isosteric heats of adsorption than copolymer HT 19 0.5/10. The T_g values for all copolymers studied are similar.

[1] P. Wieczorek, B. N. Kolarz, H. Galina, Angew. Makromol. Chem. **126** (1984) 39

[2] H. Galina, B. Kolarz, P. Wieczorek, M. Wojaczyńska, Br. Polym. J. **17** (1985) 215

[3] P. Wieczorek, M. Ilavský, B. Kolarz, K. Dušek, J. Appl. Polym. Sci. **27** (1982) 277

[4] R. Sanetra, B. Kolarz, A. Włochowicz, Polymer (in press)

[5] R. Sanetra, B. Kolarz, A. Włochowicz, Modified Polymers, Conf. Proc. Bratislava 1984, 261

[6] R. Sanetra, B. Kolarz, A. Włochowicz, Proceedings in chromatography in Poland during the last years (pol.), PAN, Lublin 1984, p. 191

[7] S. Prager, J. Chem. Phys. **33** (1960) 122

[8] J. Hradil, F. Švec, J. Chromatogr. **287** (1984) 67

[9] J.-M. Braun, J. E. Guillet, Macromolecules **9** (1976) 617

[10] M. Eder, A. Włochowicz, B. Kolarz, Angew. Makromol. Chem. **126** (1984) 81

[11] D. D. Desponde, O. S. Tyagi, Macromolecules **11** (1970) 746

[12] P. M. Zado, J. Fabacic, J. Chromatogr. **51** (1978) 37

[13] G. Dipaola-Baranyi, J.-M. Braun, J. E. Guillet, Macromolecules **11** (1978) 224

[14] G. Dipaola-Baranyi, J. E. Guillet, Macromolecules **11** (1978) 228