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Determination of solubility parameters of poly(epichlorohydrin) and poly(glycidyl azide) networks

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The solubility parameters of networks based on poly(glycidyl azide) (PGA) and poly(epichlorohydrin) (PECH) were determined via swelling experiments in a series of solvents. Because of having the same main chain structure, it was observed that PECH and PGA networks acquired the same solubility parameter value. This can be interpreted as the substitution of pendant ($-N_3$) groups for (–Cl) groups on PECH-diol main chain not having any marked effect on the solubility parameter value of PECH gel. The solubility parameters of these two polymers were also computed according to the group contribution method. A comparison of the experimentally determined solubility parameter of PGA and its calculated value implied that the pendant nitrogens are linked linearly to each other.

(Keywords: poly(glycidyl azide); poly(epichlorohydrin); solubility parameters)

INTRODUCTION

Poly(glycidyl azide)diol, PGA-diol, is a low molecular weight ($\bar{M}_n = 2000$) and difunctional hydroxyl-terminated liquid prepolymer which was recently developed for use as high energetic polymeric binder and performance improving additive in the preparation of solid rocket propellants. PGA-diol can be synthesized by the reaction of its precursor poly(epichlorohydrin)diol (PECH-diol) with sodium azide (NaN_3)[1–7]. Both PECH-diol and PGA-diol can be cured with the –NCO groups from any isocyanate, and cross-linked with any polyol compound (trimethylol propane, triethanolamine, etc.) via their hydroxyl end groups. It may be interesting to observe the effect of the substitution of $-N_3$ groups for –Cl groups on the solubility parameter of PECH gel.

The solubility parameter of polymers can be determined from the swelling data obtained in a series of solvents having nearly the same chemical character from the viewpoint of hydrogen bonding, dispersion and polarity. In addition, various methods such as inverse gas chromatography, limiting viscosity measurements, turbidimetric determination, surface tension, etc., have been developed and used successfully for the determination of the solubility parameter of polymers[8]. Besides these experimental methods, another approach to calculate the solubility parameter of both solvents and polymers is based on the group contribution method. This method is mainly dependent on the additivity properties of the cohesive energy contribution of the known functional groups of any compound[9].

The object of this study was to determine the solubility parameters of both PECH and PGA networks by swelling measurements and to obtain the effect of the substitution of $-N_3$ for –Cl groups on the solubility parameter value of the PECH network.

EXPERIMENTAL

Materials

PECH-diol was purchased from 3M (USA) under the trade name of HX-102. The number-average molecular weight ($\bar{M}_n$) was determined as $1810\,g\,mol^{-1}$ using a Knauer-type vapour phase osmometer (VPO) and benzyl ($MW = 210.23$) as a calibration standard. The OH equivalent of PECH-diol was determined as $1.14\,mEq\,g^{-1}$ ($\approx 2\,Eq\,mol^{-1}$) according to the method cited by Dee *et al.*[10] using *N*-methylimidazole as an acetylation catalyst. The viscosity was determined as 1.06×10^5 cp at 25°C using a Brookfield-type viscometer, and the density was determined as $1.36\,g\,cm^{-3}$ at 25°C. The molecular formula of PECH-diol is

$$HO\text{–}(CH_2\text{–}\underset{\displaystyle CH_2\text{–}Cl}{\underset{|}{CH}}\text{–}O\text{–})_nH$$

PGA-diol was synthesized by the nucleophilic substitution reaction of PECH-diol with sodium azide. The $\bar{M}_n$ and OH equivalent of PGA were determined to be $2220\,g\,mol^{-1}$ and $0.93\,mEq\,g^{-1}$ ($\approx 2\,Eq\,mol^{-1}$), respectively. The viscosity was determined to be 2.4×10^3 cp, and

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the density was $1.29\,g\,cm^{-3}$ at 25°C. The molecular formula of PGA is

$$HO-(CH_2-\underset{\displaystyle CH_2-N_3}{\underset{|}{CH}}-O-)_nH$$

Trimethylolpropane (TMP) and isophorone diisocyanate (IPDI) were supplied from Aldrich and Fluka, respectively, at better than 98% purity. All of the solvent used for the swelling tests of networks was better than 99% pure.

Preparation of PGA networks

For the preparation of PGA networks, TMP (as a cross-linker) was first dissolved in previously degassed PGA at 65°C and mixed for 15 min under a 200 mmHg vacuum. After addition of the required amount of IPDI, the mixture was mixed for 3 min at the same temperature and poured into Teflon moulds to obtain a film having a thickness of 1.5 mm. The mixture was cured under N_2 atmosphere at 65°C for 7 days. PECH networks were prepared with the same procedure as described above. The NCO/OH equivalent ratio was taken as 0.9 for the PGA network and 0.8 for the PECH network. The equivalent ratio of $OH_{TMP}/(OH_{TMP} + OH_{POLYMER})$ was taken as 0.4 in the preparation of PGA and PECH networks[11,12].

Determination of equilibrium swelling

Swelling measurements were performed in various solvents, listed in the caption to *Figure 1*. About 0.3 g of weighted samples of networks was immersed in various solvents until equilibrium was attained. The swollen gels were removed from the solvents, quickly blotted with a dry filter paper and weighed.

The equilibrium swelling ratio of networks was determined gravimetrically, assuming the additivity of volume through the following equation:

$$Q = 1 + (w_2/w_1 - 1)\rho_2/\rho_1 \qquad (1)$$

where Q is the swelling ratio of networks by volume, w_1 is weight of the network before swelling, w_2 is the weight of the network at equilibrium swelling, and ρ_1 and ρ_2 are the densities of the solvent and polymer, respectively.

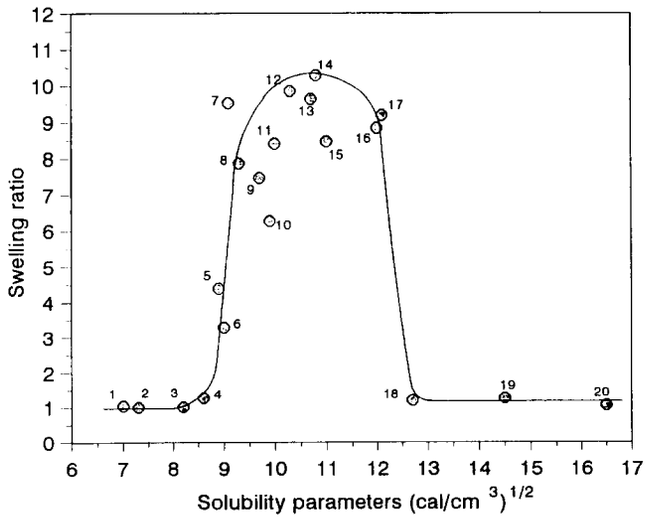


Figure 1 The relationship between the swelling ratio of PECH network and the solubility parameters of various solvents. 1, n-pentane; 2, n-hexane; 3, cyclohexane; 4, carbon tetrachloride; 5, toluene; 6, vinyl acetate; 7, tetrahydrofuran; 8, chloroform; 9, dichloromethane; 10, acetone; 11, dioxane; 12, aniline; 13, pyridine; 14, dimethylacetamide; 15, epichlorohydrin; 16, dimethyl sulfoxide; 17, dimethylformamide; 18, ethanol; 19, methanol; 20, glycerine

RESULTS AND DISCUSSION

According to Gee's theory[13] the solubility of a polymer in any solvent strongly depends on the square of the difference between their solubility parameter values, i.e. $(\delta_1 - \delta_2)^2$; here δ_1 and δ_2 are the solubility parameters of the solvent and polymer, respectively. This $(\delta_1 - \delta_2)^2$ value should be as small as possible for good solubility of a polymer in any solvent. This can be represented for any network through the following equation[13,14]:

$$Q/Q_{max} = \exp[-\alpha Q(\delta_1 - \delta_2)^2] \qquad (2)$$

where Q_{max} is maximum swelling ratio and α is a constant. Equation (2) can be rearranged as follows:

$$[Q^{-1}\ln(Q_{max}/Q)]^{1/2} = |\alpha^{1/2}(\delta_1 - \delta_2)| \qquad (3)$$

According to equation (3), a plot of $[Q^{-1}\ln(Q_{max}/Q)]^{1/2}$ *versus* the solubility parameters of a series of solvents will give $\alpha^{1/2}$ and δ_2 values from the slope and intersection of the horizontal axis of obtained line, respectively. Equation (3) was recently used for the determination of the solubility parameters of *N*-isopropyl acrylamide and poly(dimethylsiloxane) networks[15,16]. In order to apply this method, the equilibrium swelling values of PECH networks in various solvents were determined (*Figure 1*). PECH gel exhibited the largest equilibrium swelling ratio in dimethylacetamide $\delta_1 = 10.80\ (cal\,cm^{-3})^{1/2}$, and from the plot of the quantities on the left-hand side of equation (3) against δ_1, the solubility parameter of PECH gel and the constant α were obtained as $\delta_{PECH\,gel} = 10.9\ (cal\,cm^{-3})^{1/2}$ and $\alpha = 0.12\,cm^3\,cal^{-1}$ by using the least squares regression method (*Figure 2*). The solubility parameters and densities of the solvents used in swelling experiments on both PECH and PGA networks were obtained from Bandrup and Immergut[17].

The contribution of dispersion, polar and hydrogen bonding interactions to the solubility parameter of PECH gel was determined by the same method

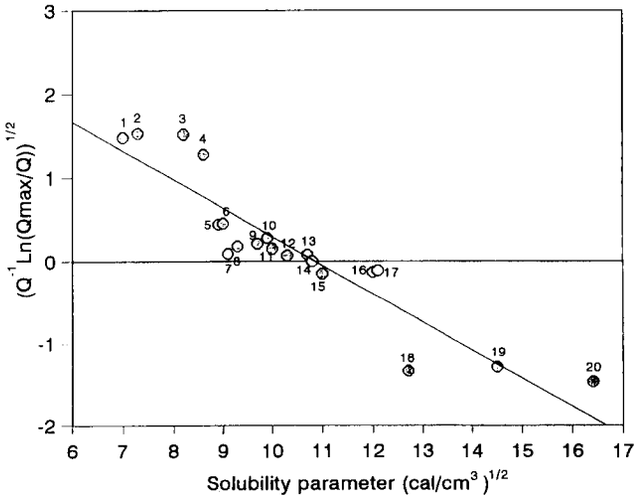


Figure 2 Linear plot of $[Q^{-1}\ln(Q_{max}/Q)]^{1/2}$ *versus* the solubility parameter of the solvents shown in *Figure 1* for the PECH network. The correlation coefficient is 0.921

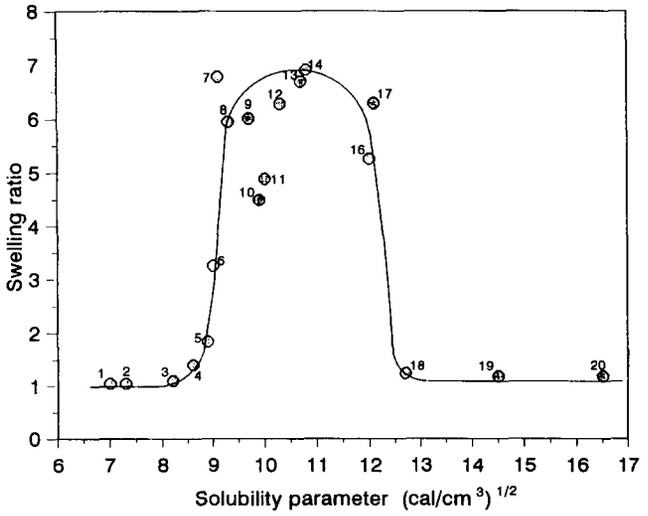


Figure 3 The relationship between the swelling ratio of the PGA network and the solubility parameters of various solvents shown in *Figure 1*

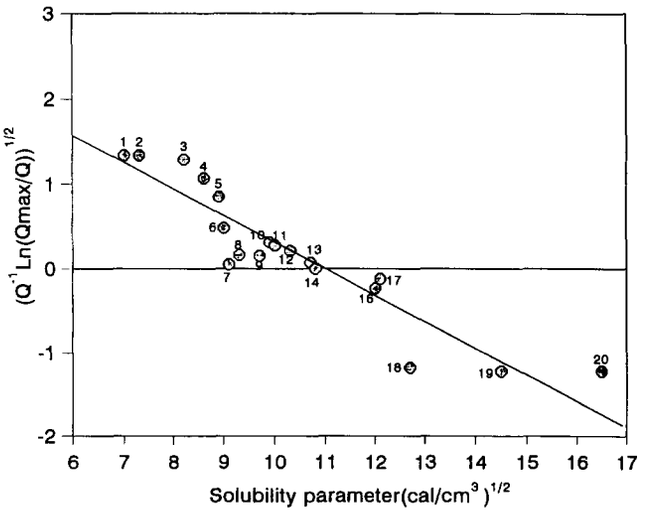
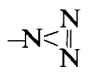


Figure 4 Linear plot of $[Q^{-1}\ln(Q_{max}/Q)]^{1/2}$ *versus* the solubility parameters of the solvents shown in *Figure 1* for the PGA network. The correlation coefficient is 0.927

as $\delta_{D,PECH\,gel} = 9.3\,(cal\,cm^{-3})^{1/2}$, $\delta_{P,PECH\,gel} = 5.5\,(cal\,cm^{-3})^{1/2}$ and $\delta_{H,PECH\,gel} = 4.5\,(cal\,cm^{-3})^{1/2}$, respectively. These results showed that the main contribution was due to dispersion forces. The solubility parameter of linear PECH-diol was calculated by the group contribution method as $\delta_{PECH\text{-}diol} = 11.2\,(cal\,cm^{-3})^{1/2}$ using the values of Fedors[9]. As can be seen from these results, the solubility parameter of PECH as determined from swelling experiments and calculated by the group contribution method are in very good accordance.

Figure 3 shows the relationship between the swelling ratio of PGA gel and the solubility parameters of a series of solvents. As observed from *Figure 3*, PGA gel exhibited the largest swelling ratio in dimethylacetamide, as did PECH gel. According to equation (3), the solubility parameter and $\alpha^{1/2}$ value of PGA gel were determined from the linear plot of $[Q^{-1}\ln(Q_{max}/Q)]^{1/2}$ *versus* the solubility parameters of solvents. From the plot they were calculated as $\delta_{PGA\,gel} = 11.0\,(cal\,cm^{-3})^{1/2}$ and $\alpha = 0.10\,cm^3\,cal^{-1}$ (*Figure 4*). The contribution of dispersion, polar and hydrogen bonding type interactions in the PGA network was determined as $\delta_{D,PGA\,gel} = 10.4\,(cal\,cm^{-3})^{1/2}$, $\delta_{P,PGA\,gel} = 5.6\,(cal\,cm^{-3})^{1/2}$ and $\delta_{H,PGA\,gel} = 4.7\,(cal\,cm^{-3})^{1/2}$ from the linear plot of swelling data. These results showed that the main contribution was due to dispersion forces. The solubility parameter value of linear PGA-diol was calculated by the group contribution method using the values of Fedors[9]. It was reported earlier that the nitrogen atoms within the azide group are attached linearly with ionic and covalent bonds[18,19].

By assuming the pendant nitrogen atoms of PGA to be attached in a cyclic form, that is,



the solubility parameter value was calculated as 15.8 $(cal\,cm^{-3})^{1/2}$, but taking into consideration the linear attachment of pendant nitrogen atoms (i.e. $-N{=}N^{+}{=}N^{-}$) within PGA, the solubility parameter value of PGA was calculated as 12.2 $(cal\,cm^{-3})^{1/2}$, which is in moderate accordance with the experimentally determined value (i.e. $\delta_{PGA\,gel} = 11.0\ (cal\,cm^{-3})^{1/2}$). These results can be taken as further proof of the linear attachment of pendant nitrogen atoms within PGA.

In spite of the difference between the NCO/OH equivalent ratio of PECH and PGA gels, their experimentally determined solubility parameters are nearly the same, and they have the same swelling behaviour. In conclusion, it may be noted that the effect of the conversion of PECH into PGA does not have much effect on the solubility parameter of PECH.

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