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Determination of solubility parameters of cross-linked macromonomeric initiators based on polypropylene glycol

Abdulkadir Allı [a], Baki Hazer [a,*], Bahattin M. Baysal [b]

[a] Zonguldak Karaelmas University, Department of Chemistry, 67100 Zonguldak, Turkey
[b] Bogazici University, Department of Chemical Engineering, 80815 Bebek-Istanbul, Turkey

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Abstract

A new type macromonomeric azo initiators also named macroinimers, MIMs, based on polypropylene glycol, PPG, with molecular weight 400 and 2000, were synthesized. Self-condensing radical polymerization of the macroinimers gave cross-linked polypropylene glycols. The solubility parameters of the cross-linked polymers determined using swelling experiments in a series of solvents have been reported. Crosss-linked PPG-400 and cross-linked PPG-2000 indicated the same solubility parameter value. But their swelling ratios were different because of the differences of the chain lengths in between of the cross-points (Mc) of the gels. Therefore, while the largest swelling ratio exhibited by a cross-linked PPG-2000 in tetrahydrofurane was being 19.48, this ratio was 6.84 for the cross-linked PPG-400 in the same solvent. The solubility parameters and constant α for these cross-linked polymers were obtained as $\delta_{\text{cross-linked PPG-400}} = 9.56$ $(\text{cal cm}^{-3})^{1/2}$, $\alpha = 0.123\ \text{cm}^3\ \text{cal}^{-1}$ and $\delta_{\text{cross-linked PPG-2000}} = 8.95$ $(\text{cal cm}^{-3})^{1/2}$, $\alpha = 0.107\ \text{cm}^3\ \text{cal}^{-1}$ by using the least squares regression method.

Keywords: Macroinimer (macromonomeric initiator); Cross-linked polypropyleneglycol (cross-linked PPG); Self-condensing radical polymerization (SCRP); Solubility parameter

1. Introduction

Several macroazoinitiators based on polyethylene glycol, PEG, and azo functions have been used with some success in block/graft copolymerizations via free radical mechanism [1–6].

Three functional macromonomeric initiator (macroinimer) which behave as an initiator, macromonomer and a crosslinker, can be derived from macroazoinitiator via capping reactions of hydroxyl ends with methacryloyl chloride [7–10]. Macromonomeric initiators initiate the bulk or dispersion polymerization of a vinyl monomer leading to highly branched or cross-linked block/graft copolymers [11–15]. Macroinimer concentration and polymerization time are effective to obtain polymers from highly branched to cross-linked. In addition, gelation properties by means of swelling ratios of the cross-linked

* Corresponding author. Tel.: +90 372 2572070; fax: +90 372 2574181.
E-mail addresses: bkhazer@karaelmas.edu.tr, bhazer2@yahoo.com (B. Hazer).

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copolymers obtained by both macroinimers and macrocrosslinkers were compared [16]. In this manner, self-condensing ATRP of poly(tert-butyl acrylate), PtBA, macroinimer ($M_n = 3060$) led to hyperbranched or highly branched PtBA with M_n at around 80,000 instead of cross-linked polymer [17]. Similarly, self-condensing group transfer [18], self-condensing ATRP [19], and self-condensing nitroxy mediated [20] living radical polymerizations of monomeric initiators (inimers), in order to obtain higher branched polymers or dendrimers, have been reported.

Macroinimers can also thermally homopolymerize by themselves. However, the solubility parameters and the swelling behaviors of these cross-linked macroinimers obtained by self-condensing radical polymerization were not studied. 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 view point of hydrogen bonding, dispersion and polarity. A method often used for cross-linked polymers and applicable to partially crystalline material is based on an evaluation of maximum in swelling using a series of solvents of varying and known solubility parameters [21,22]. Various methods such as inverse gas chromatography, limiting viscosity measurements, turbidimetric determination, surface tension [23] and contribution method [24] have been developed and used successfully for the determination of the solubility parameter of polymers.

The object of this study was to determine the solubility parameters of cross-linked macroinimers based on polypropylene glycol networks and to compare the effect of the chains length of these polymer networks via swelling measurements.

2. Experimental

2.1. Materials

4,4′-azobis-4-cyanopentanoic acid (ACPA) was purchased from Fluka AG and poly(propylene glycol) bis (2-aminopropyl ether) (PPG-NH_2) (amine groups at both ends of each chain) of average MW 400 and MW 2000 were gifts from Huntsman Corp. (Switzerland). The solvents in this experimental are listed in Table 1. All these chemically pure solvents and other reagents were extra pure products. 4,4′-Azobis-4-cyanopentanoyl chloride (ACPC) was prepared by the reaction of ACPA with phosphorus pentachloride. The reaction was carried out in

Table 1
Solvents used in this work and their solubility parameters

Solvent	δ (cal/cm^3)$^{1/2}$	δ (MPa)$^{1/2}$	δ_d (cal/cm^3)$^{1/2}$	δ_p (cal/cm^3)$^{1/2}$	δ_h (cal/cm^3)$^{1/2}$
n-Hexane	7.3	14.9	7.30	0	0
Cyclohexane	8.2	16.8	8.20	0	0.098
Carbon tetrachloride	8.6	17.6	8.70	0	0.29
Toluene	8.9	18.2	8.80	0.68	0.98
Vinyl acetate	9.0	18.4	–	–	–
Ethylacetate	9.1	18.6	7.73	2.59	3.52
Tetrahydrofurane	9.1	18.6	8.22	2.79	3.91
Benzene	9.2	18.8	9.00	0	0.98
Chloroform	9.3	19.0	8.71	1.52	2.79
Benzaldehyde	9.4	19.2	9.50	3.62	2.59
Methylene chloride	9.7	19.8	8.92	3.09	2.99
Bromobenzene	9.9	20.3	9.90	2.68	2.00
Acetone	9.9	20.3	7.56	4.88	3.41
1,4-Dioxane	10.0	20.5	9.27	0.88	3.61
Acetic acid	10.1	20.7	7.07	3.90	6.59
Acetaldehyde	10.3	21.1	7.17	3.90	5.51
2-Propanol	11.5	23.5	7.73	2.99	8.03
Acetonitrile	11.9	24.3	7.49	8.81	2.99
Dimethylformamide	12.1	24.8	8.49	6.68	5.51
1,4-Bütandiol	12.1	24.8	–	–	–
Ethyl alcohol	12.7	26.0	7.72	4.30	9.48
Methanol	14.5	29.7	7.37	6.00	10.89
Glycerol	16.5	33.8	8.50	5.91	14.31
Water	23.4	47.9	7.57	7.82	20.71

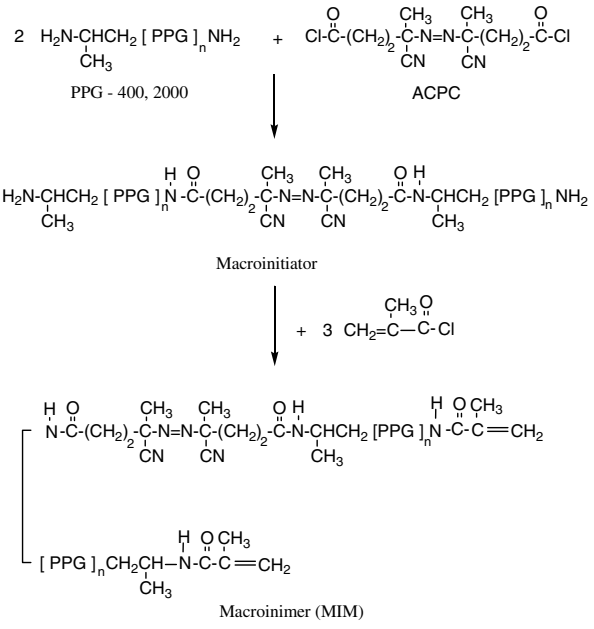
benzene at room temperature. The filtration and purification procedure were applied as described in the literature [25].

2.2. Characterization

IR-spectra of the macroazoinimers were taken using a Jasco 300 E IR spectrometer. ^{1}H NMR spectra of the products were recorded by a Bruker Avance DPX 400 MHz NMR spectrometer. Gel permeation chromatography (GPC) was used to determine molecular weights of the samples and their distributions with Knauer eurogel columns B71, B72 and B73 were used. Polystyrene standards of low polydispersity were used to generate a calibration curve.

2.3. Synthesis of macroinimer

Macroinimer (MIM) containing PPG units was synthesized. The steps in the reaction and the products obtained can be seen in Scheme 1. In a typical procedure for MIM, a solution of 2.0 g (6.3 mmol) of ACPC in 50 mL $CHCl_3$ was added to the mixture of 25.24 g (12.6 mmol) of poly(propylene) bis (2-aminopropyl ether) (PPG-NH_2-2000) and 10 mL of aqueous NaOH (20 wt%) and stirred for 24 h at room temperature. The molar ratio of ACPC to PPG-2000 was 1:2. After the reaction, the mixture was washed with water three times to secure the removal of salts and ACPA from the product. The organic phase was dried with Na_2SO_4 overnight at 0 °C. Solvent was evaporated. Yellow viscous liquid (macroinitiator) was dried under vacuum and stored at 0 °C until use. The Yield was 91%.



Scheme 1. Synthesis of macroinimer.

The second step in the synthesis of MIM is the addition of methacryloyl chloride macroinitiator obtained. The yellow viscous liquid in 10 mL of aqueous NaOH (20 wt%) was mixed with methacryloyl chloride in $CHCl_3$. The molar ratio of macroinitiator to methacryloyl chloride was 1/3. The reaction mixture was stirred for 24 h and after reaction the mixture was washed with water and the product (MIM) was dried with Na_2SO_4. After evaporation of solvent, it was dried and stored in a refrigerator. The yields of MIM-PPG-400 and MIM-PPG*2000 were 89 and 78 wt%, respectively.

2.4. Preparation of cross-linked PPG

For the preparation of cross-linked PPG, the macroinimer was spread into a petri dish and carried out on this glass plate by introduction to an oven preheated to 90 °C for 10 h. The crude gel was immersed into the chloroform and separated from soluble part; then dried under vacuum at 30 °C for 48 h.

2.5. Determination of the equilibrium swelling ratio

The swelling ratio of cross-linked PPG at equilibrium in each solvent was measured at 25 °C. Dried cross-linked PPG was immersed in each solvent at 25 °C for 24 h. The sample was removed from each solvent and was frequently weighted after trapped with a filter paper to remove excess solvent on the surface. The equilibrium swelling ratio (Q) of cross-linked polymers was determined gravimetrically, assuming the additivity of volume through the following equation [26]:

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

where Q is the swelling ratio of cross-linked polymers 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.

3. Results and discussion

3.1. Synthesis of macroinimers

PPG Macroinimers were sequentially synthesized from the reaction of ACPC and PPG-NH_2-400 and 2000 with a molar ratio of 1:2 then methacryloyl chloride was capped with the terminal amine groups of the polyazoesters obtained. Scheme 1 shows the synthesis reactions of MIM-PPG-400 and MIM-PPG-2000. The macroinimer overall yield was at around 91 wt%. Molecular weights (M_n): 1044 (theoretical) and 1395 (from GPC, MWD = 1.661) for MIM-PPG-400; 4380 (theoretical) and 3867 (from GPC, MWD = 1.393). IR and ^{1}H NMR spectra of the macroinimer confirmed the expected structure of the products. Fig. 1 shows the IR transmittance spectrum of MIM-PPG obtained. The characteristic peaks of MIM-PPG were observed at 3500 cm^{-1} for –NH stretching vibration band, at 1110 cm^{-1} for C–O–C stretching vibration band, at 1660 cm^{-1} for carbonyl absorption. The ^{1}H NMR spectrum of macroinimer MIM-PPG confirms the structural formula. In Fig. 2, we observed the signals of the $–CH_3$ groups (at δ 1.2), $–CH_2$ groups (at δ 3.4–3.6) of PPG and vinyl $–CH_2$ groups (at δ 5.6). $–CH_2$groups (at δ 2.25–2.4) of ACPA [23]. The signals that appeared at 4.10 ppm due to –NH groups in the macroinimer.

3.2. Cross-linked formation with MIM

Self-condensing radical polymerization of the macromonomeric initiators were carried out at 90 °C for 10 h. A small amount of MIM decomposes into macromonomer radicals which start free radical polymerization of vinyl ends of undecomposed MIM which behaves as a macrocrosslinker, and then a cross-linked copolymer is formed.

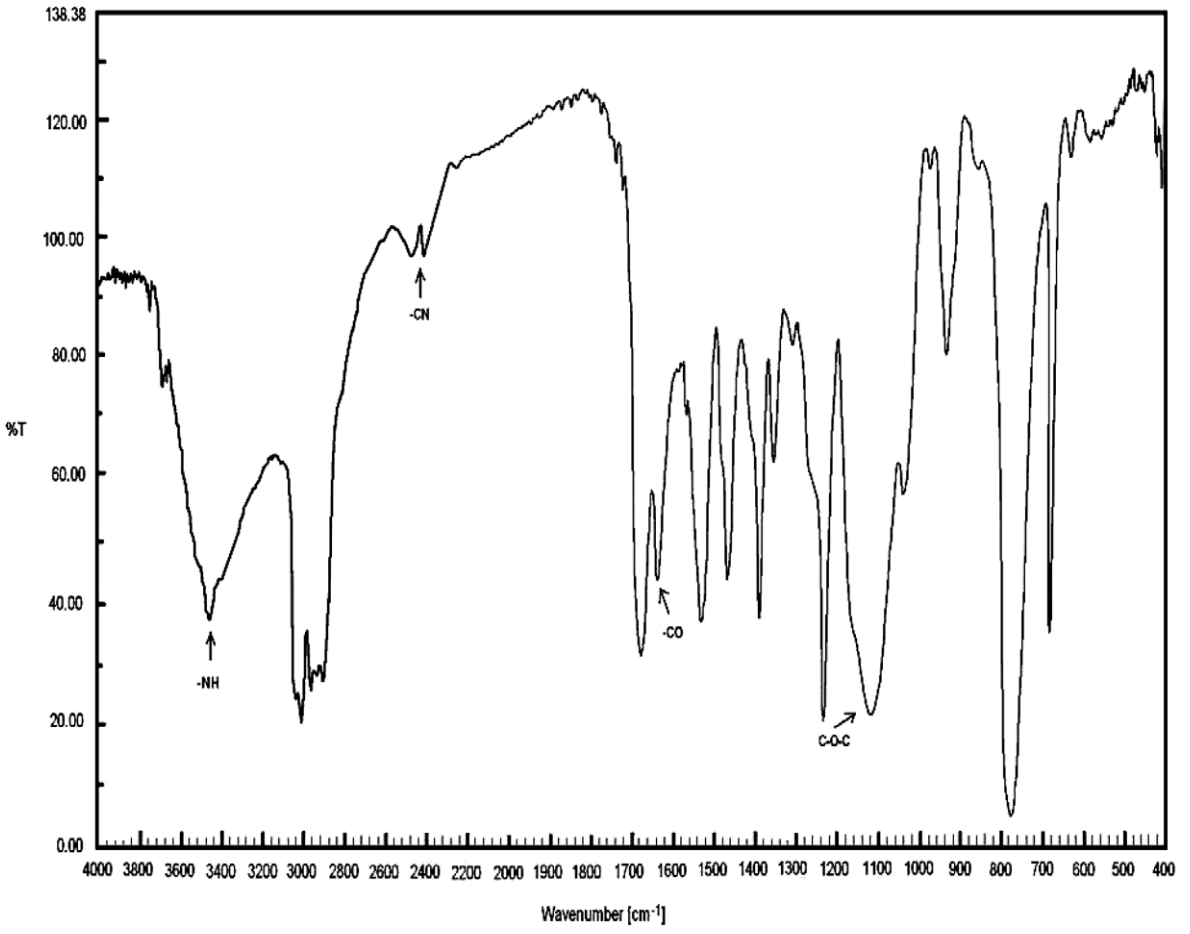


Fig. 1. IR spectrum of macroazoinimer MIM-PPG-400.

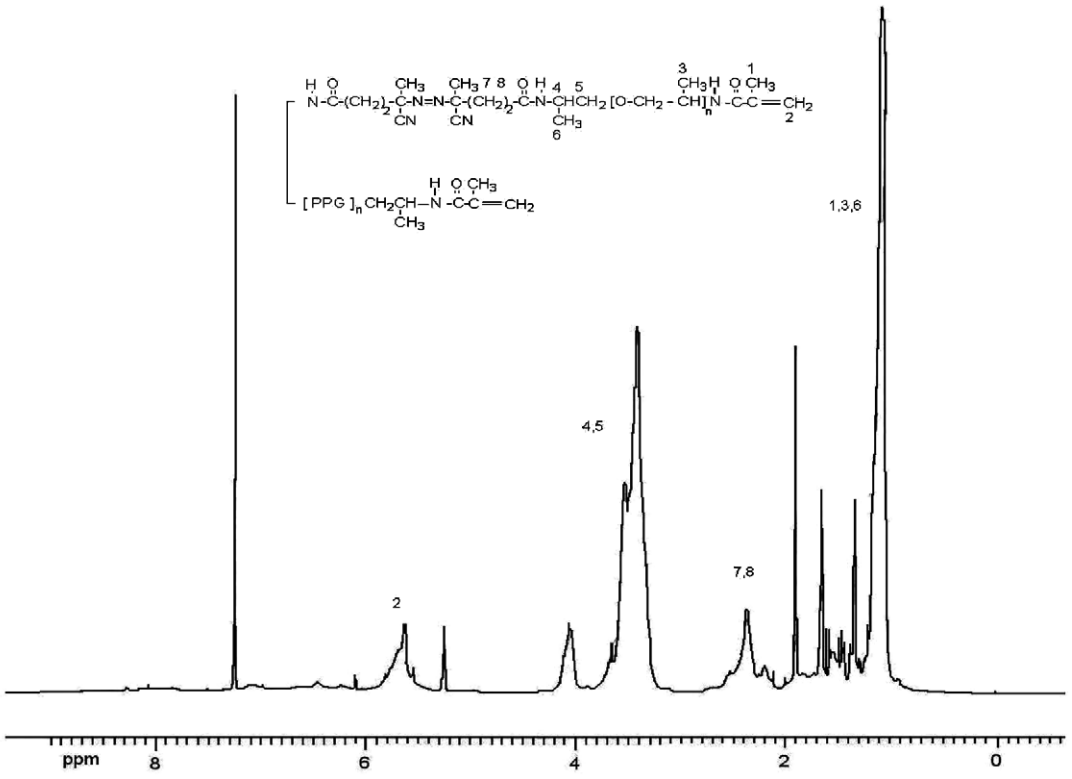


Fig. 2. ^{1}H NMR spectrum of macroazoinimer MIM-PPG-400.

Scheme 2 shows the cross-linking formation of the PPG macroinimers. Sol–gel analysis of the cured MIM-PPG-400 and 2000 indicated 40 and 34 wt% of gel polymer, respectively. The soluble part (GPC results: $M_n = 1898$, MWD = 1.35 for MIM-PPG-400 and $M_n = 4756$, MWD = 1.23 for MIM-PPG-2000) was dimer-trimers of the PPG segments probably arising from the partly degradation of MIMs at 90 °C. The gelation behaviour of a macroinimer can be explained as follows. A small amount of MIM decomposes into macromonomer radicals which start free radical polymerization of vinyl ends of MIM, and a cross-linked copolymer is formed. We can conclude that the chain transfer reactions of the radicals formed cause to the low conversion of gel polymer. At that point, soluble part of the macroinimer does not have azo groups and is not active any more.

3.3. Determination of solubility parameter

The solubility parameter is defined as the square root of the energy of vaporization per unit volume of material and is given by the symbol δ [27].

$$\delta = (\Delta Ev/V)^{1/2}(\mathrm{cal}^{1/2}\,\mathrm{cm}^{-3/2}) \text{ or } (\mathrm{MPa})^{1/2}$$

Thus δ is proportional to the cohesion of the material or the strength of attraction between molecules making up the material. A method often used for cross-linked polymers and applicable to partially crystalline material is based on an evaluation of maximum in swelling using a series of solvents of varying and known solubility parameters.

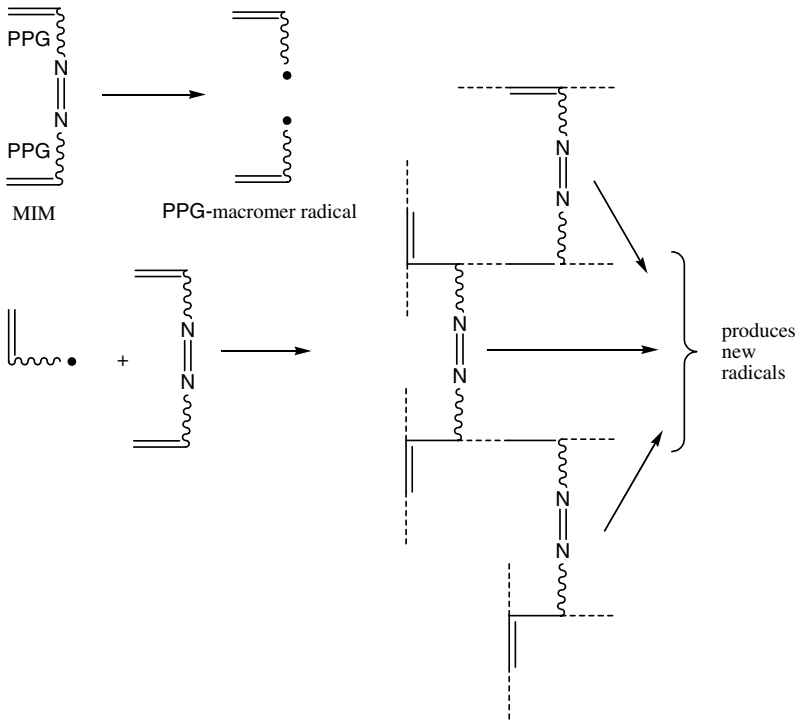
The solubility of a polymer in any solvent strongly depends on the square of the difference between their solubility parameter values. This value should be as small as possible for good solubility of a polymer in any solvent. The following relation was used for this purpose [21,28].

$$Q/Q_{\max} = \exp(-\alpha Q(\delta_{\text{solvent}} - \delta_{\text{polymer}})^2) \quad (1)$$

Eq. (1) can be rearranged as

$$(Q^{-1}\ln(Q_{\max}/Q))^{1/2} = \alpha^{1/2}(\delta_{\text{solvent}} - \delta_{\text{polymer}}) \quad (2)$$

According to Eq. (2), 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_{polymer} values from the slope and intersection of the horizontal axis of obtained



Scheme 2. Cross-linking formation with macroinimer based on polypropylene glycol.

line, respectively. Eq. (2) was recently used for the determination of the solubility parameters of *N*-isopropyl acrylamide [29], poly(dimethylsiloxane) networks [30], poly(epichlorohydrin) and poly(glycidyl azide) networks [31].

In order to apply this method, the equilibrium swelling values of crs PPG in various solvents were determined. Fig. 3 shows the relationship between the swelling ratio of the crs PPG-400 and the solubility parameter of various solvents. crs PPG-400 exhibited the largest swelling ratio ($Q = 6.84$) in THF $\delta = 9.10$ $(\text{cal cm}^{-3})^{1/2}$, and from the plot of the quantities on the left-hand side of Eq. (2) against δ_{solvent}, the solubility parameter of crs PPG-400 and the constant α were obtained as $\delta_{\text{crs PPG-400}} = 9.56$ $(\text{cal cm}^{-3})^{1/2}$ and $\alpha = 0.123\ \text{cm}^3\ \text{cal}^{-1}$ by using the least squares regression method (Fig. 4). The solubility parameters of the solvents used in swelling experiments on both crs PPG-400 and crs PPG-2000 were obtained from Bandrup and Immergut [32].

Fig. 5 shows the relationship between the swelling ratio of cross-linked PPG-2000 and solubility parameters of a series of solvents. As observed from Fig. 3, cross-linked PPG-2000 exhibited the largest swelling ratio ($Q = 19.48$) in THF. According to

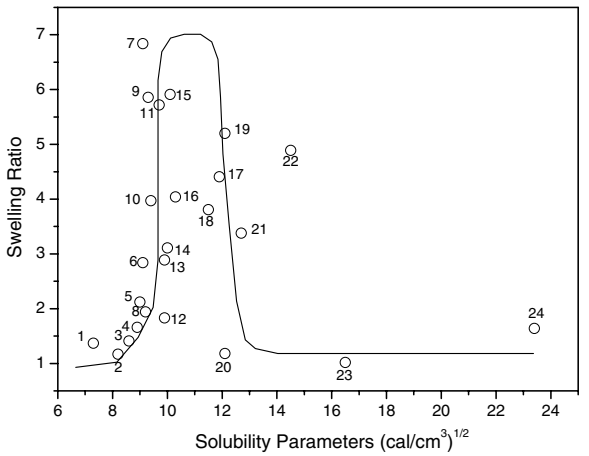


Fig. 3. The relationship between the swelling ratio of cross-linkedPPG-400 and solubility parameters of various solvents. 1, *n*-hexane; 2, cyclohexane; 3, carbon tetrachloride; 4, toluene; 5, vinyl acetate; 6, ethylacetate; 7, tetrahydrofuran; 8, benzene; 9, chloroform;10, benzaldehyde; 11, methylene chloride; 12, bromobenzene; 13, acetone; 14, 1,4-dioxane; 15, acetic acid; 16, acetaldehyde; 17, 2-propanol; 18, acetonitrile; 19, dimethylformamide; 20, 1,4-butandiol; 21, ethyl alcohol; 22, methanol; 23, glycerol; 24, water.

Eq. (2), the solubility parameter and $\alpha^{1/2}$ value of cross-linked PPG-2000 were determined from the

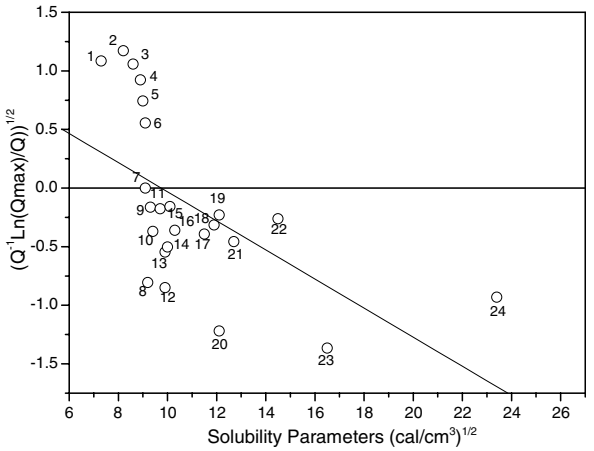


Fig. 4. Linear plot of $[Q^{-1}\ln(Q_{max}/Q)]^{1/2}$ versus the solubility parameter of the solvents shown in Fig. 1 for the cross-linked PPG-400.

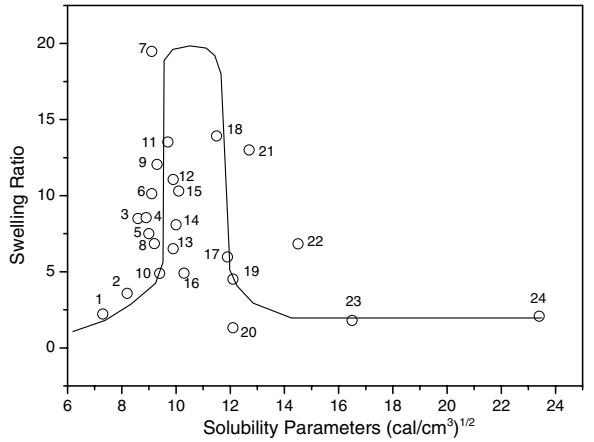


Fig. 5. The relationship between the swelling ratio of cross-linked PPG-2000 and solubility parameters of various solvents. 1, *n*-hexane; 2, cyclohexane; 3, carbon tetrachloride; 4, toluene; 5, vinyl acetate; 6, ethylacetate; 7, tetrahydrofuran; 8, benzene; 9, chloroform;10, benzaldehyde; 11, methylene chloride; 12, bromobenzene; 13, acetone; 14, 1,4-dioxane; 15, acetic acid; 16, acetaldehyde; 17, 2-propanol; 18, acetonitrile; 19, dimethylformamide; 20, 1,4-butandiol; 21, ethyl alcohol; 22, methanol; 23, glycerol; 24, water.

linear plot of $(Q^{-1}\ln(Q_{max}/Q))^{1/2}$ versus the solubility parameters of solvents. From the plot they were calculated as $\delta_{\text{cross-linked PPG-2000}} = 8.95\ (\text{cal cm}^{-3})^{1/2}$ and $\alpha = 0.107\ \text{cm}^3\ \text{cal}^{-1}$ (Fig. 6).

Cohesive energy is also dependent on the interaction between polar groups and hydrogen bonding. In these cases the solubility parameter corresponds with the total cohesive energy. Formally, the cohesive energy may be divided into three parts,

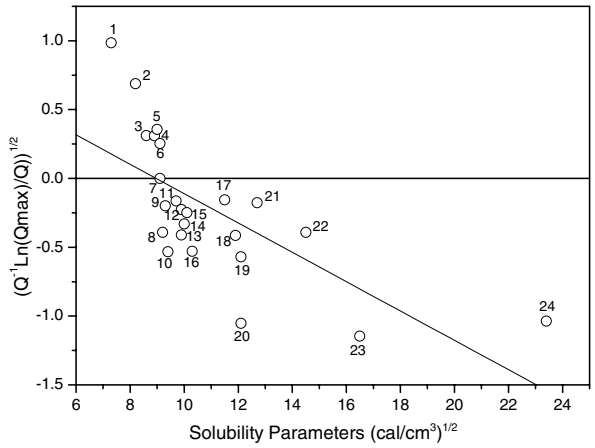


Fig. 6. Linear plot of $[Q^{-1}\ln(Q_{max}/Q)]^{1/2}$ versus the solubility parameter of the solvents shown in Fig. 1 for the cross-linked PPG-2000.

corresponding with three types of interaction forces [33].

$$E_{coh} = E_d + E_p + E_h$$

and the corresponding equation for the solubility parameter is

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

where δ_d = contribution of dispersion forces; δ_p = contribution of polar forces and δ_h = contribution of hydrogen bonding. The contribution of dispersion, polar and hydrogen bonding interactions to the solubility parameter of cross-linked PPG-400 and cross-linked PPG-2000 were determined by the same method as $\delta_{\text{d,cross-linked PPG400}} = 8.42\ (\text{cal cm}^{-3})^{1/2}$, $\delta_{\text{p,cross-linked PPG-400}} = 4.60\ (\text{cal cm}^{-3})^{1/2}$, $\delta_{\text{h,cross-linked PPG-400}} = 8.32\ (\text{cal}^{-3})^{1/2}$, as $\delta_{\text{d,cross-linked PPG-2000}} = 7.69\ (\text{cal}^{-3})^{1/2}$, $\delta_{\text{p,crs PPG-2000}} = 4.0\ (\text{cal}^{-3})^{1/2}$ and $\delta_{\text{h,cross-linked PPG-2000}} = 7.06\ (\text{cal}^{-3})^{1/2}$, respectively. These results showed that the main contributions were due to dispersion forces and hydrogen bonding. The contribution of polar part of solubility parameter can be negligible.

4. Conclusions

The solubility parameters of cross-linked macroinimers based on polypropylene glycol networks were determined by swelling measurements. Cross-linked PPG-2000 exhibited the larger swelling ratio than cross-linked PPG-400, because of the difference chain lengths between the cross-link points. In addition, the solubility parameters of the cross-linked polymers were found to be different from

those of their best solvents. This difference may arise from the dendrimer like crosslinking moity instead of smooth crosslinking obtained from a divinyl crosslinker. In addition, dispersion forces and hydrogen bonding are found to be influenced on the solubility parameters. Presumably,

(amide) groups in the networks can cause the hydrogen bonding.

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