Determination of the Thermodynamic Properties of Poly \([2-(3\text{-phenyl}-3\text{-methylcyclobutyl})\text{-}2\text{-hydroxyethyl methacrylate-co-methacrylic acid}]\) at Infinite Dilution by Inverse Gas Chromatography

İsmet KAYA  
Department of Chemistry, Faculty of Sciences and Arts,  
Çanakkale Onsekiz Mart University, Çanakkale-TURKEY

Kadir DEMİRELLİ  
Department of Chemistry, Faculty of Sciences and Arts,  
Fırat University, Elazığ-TURKEY

Received 20.04.1998

Some thermodynamic quantities were obtained for the interactions of poly \([2-(3\text{-phenyl}-3\text{-methylcyclobutyl})\text{-}2\text{-hydroxyethyl methacrylate-co-methacrylic acid}]\) Poly (PCHEMA-co-MA) with alcohols, ketones, acetates, aromatics and n-alkanes by inverse gas chromatography in the temperature range of 150-180°C. The specific retention volumes, \(V_g^0\), weight fraction activity coefficients of solute probes at infinite dilution, \(\Omega^0\) and Flory-Huggins thermodynamic interaction parameters, \(\chi_{12}^0\) between polymers and solvents were determined. The partial molar free energy, \(\Delta G_1^0\), the partial molar heat of mixing, \(\Delta H_1^0\), at infinite dilution and the solubility parameters of the polymer, \(\delta_2\), were calculated. The copolymer was characterized by \(^1\text{H}-\text{NMR}, \text{FT-IR} and \text{DSC} \text{analyses}

**Key Words:** Poly \([2-(3\text{-phenyl}-3\text{-methylcyclobutyl})\text{-}2\text{-hydroxyethyl methacrylate-co-methacrylic acid}]\), inverse gas chromatography, polymer-solvent interactions.

**Introduction**

The inverse gas chromatography (IGC) method has been used extensively to study the structure of polymers, the interactions of various liquids and gases with polymeric materials, and polymer-polymer miscibility. The method is simple, fast and economical and provides valuable thermodynamic information for characterization of polymeric materials\(^1\)\(^-\)\(^6\).

In this study, we examined the interactions of poly \([2-(3\text{-phenyl}-3\text{-methylcyclobutyl})\text{-}2\text{-hydroxyethyl methacrylate-co-methacrylic acid}]\) (PPCHEMA-co-MA) with solvents and the solubility parameters of PPCHEMA-co-MA by using IGC in the temperature range 150-180°C.

The probe specific retention volumes, \(V_g^0\), corrected to 0°C were calculated from the standard chromatographic relation
\[ V_2^o = \Delta t \frac{G273.2}{wT_r} 3/2[P_i/P_o] ^2 - 1/(P_i/P_o ^3 - 1) \]  

(1)

where \( \Delta t = t_p - t_g \) is the difference between the retention times of the probe, \( t_p \), and the methane, \( t_g \); \( F \) is the flow rate of the carrier gas measured at room temperature, \( T_r \); \( w \) is the mass of the polymeric stationary phase; and \( P_i \) and \( P_o \) are the inlet and outlet pressures, respectively\(^7\text{-}^{10}\).

The weight fraction activity coefficient, \( \Omega_1^\infty \), the partial molar free energy, \( \Delta G_1^\infty \), and the average partial molar enthalpy, \( \Delta H_1^\infty \), at infinite dilution of the organic solvents were calculated according to the following equations\(^3\):

\[ \Omega_1^\infty = 273.2R/V^o g P^o \exp[-P^o(B_{11} - V_1)/RT] \]  

(2)

\[ \Delta G_1^\infty = RT \ln \Omega_1^\infty \]  

(3)

\[ \Delta H_1^\infty = R\partial \ln(\Omega_1^\infty)/\partial(1/T) \]  

(4)

where \( B_{11} \) is the second virial coefficient of the organic solute in the gaseous state; \( P^o_1 \) is the vapour pressure of the probes at temperature \( T(K) \); and \( M_1 \) is the molecular weight of the probe. The values of \( P^o_1 \) and \( B_{11} \) have been calculated as in the literature\(^11\).

The molar volume of the solute, \( V_1 \), was calculated using the following relation\(^12\):

\[ V_1 = V_c/\rho_r \]  

(5)

where \( V_c \) is the critical molar volume and \( \rho_r \) is the reduced density of the solute given as

\[ \rho_r = 1.20 + (5.565 - 11.03z_c)(1 - T/T_c)(0.8z_c + 0.31) \]  

(6)

where \( z_c \) is the critical compressibility factor and \( T_c \) is critical temperature.

The Flory-Huggins parameters, \( \chi_{12}^\infty \), characterizing the interactions of a vapour-phase probe with a polymer are determined by the following equation:

\[ \chi_{12}^\infty = \ln(273.2R\nu_2/V^o g V_1 P^o_1) - 1[-P^o_1/RT(B_{11} - V_1)] \]  

(7)

where \( R \) is the gas constant and \( \nu_2 \) is the specific volume of the polymer. The solubility parameter of the probe is calculated from the relation\(^13\text{-}^{16}\).

\[ \delta_1 = [(\Delta H_v - RT)/V_1]^{0.5} \]  

(8)

The solubility parameter of the polymer, \( \delta_2 \), can be calculated by the following relation:

\[ [(\delta_1^2/RT) - \chi_{12}^\infty/V_1] = (2\delta_2/RT)\delta_1 - \delta_2^2/RT \]  

(9)

If the left-hand side of this equation is plotted against \( \delta_1 \), a straight line having a slope of \( 2\delta_2/RT \) and an intercept of \( (-\delta_2^2/RT) \) is obtained. The solubility parameter of the polymer, \( \delta_2 \), can be determined from both the slope and the intercept of the straight line\(^9\).
Experimental

Materials

Ten polar and non-polar probes were used in this study. They were selected to provide several groups of chemically different nature and polarity. N-dodecane was supplied by Aldrich Chemical Co., and methanol, ethanol, acetone, ethyl methyl ketone, methyl acetate, ethyl acetate, benzene, toluene and o-xylene of chromatographic grade were supplied by Merck Chemical Co. Chromosorb W (45-60 mesh) was supplied by Sigma Chemical Co. 1,4-Dioxane and n-hexane (Aldrich) were dried over anhydrous MgSO₄ before use. Methacrylic acid and KOH (Aldrich) were used as received. 1-chloro-2,3-epoxy-5-methyl-5-hexene was obtained from the Institute of Polymeric Materials in the Academy of Sciences of Azerbaijan and freshly distilled before use. [2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate] was synthesized via the method given for the epoxy-carboxy reactions¹⁷–²¹.

Copolymerization of the monomers

The monomer [2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate] and methacrylic acid were freed from inhibitor by washing with dilute KOH solution followed by reacting with distilled water and drying over anhydrous MgSO₄. Appropriate amounts of [2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate] and methacrylic acid and 1,4-dioxane and benzoyl peroxide (0.2% of the weight of the monomer) were placed into a reaction tube and purged with Ar for about 10 min. The sealed tube was kept at 60°C for 15 h. The PPCHEMA-co-MA was purified by reprecipitation in n-hexane from 1,4-dioxane solution and finally dried under vacuum. The yield was about 75% for PPCHEMA-co-MA.

Analysis

The molecular weight of the PPCHEMA-co-MA was determined by gel permeation chromatography using polystyrene and tetrahydrofuran as the standard and solvent, respectively. The weight-average molecular weight was found to be 45 000 g/mol (polydispersity:2.62) for PPCHEMA-co-MA. The block copolymer composition was determined by ¹H-NMR measurement. In the block copolymer, the composition of [2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate] and methacrylic acid found to be 55% and 45%, respectively. The glass transition temperature, Tg, of PPCHEMA-co-MA is found to be about 105°C by Shimadzu differential scanning calorimeter (DSC) (DSC-50 model). Density is measured by determining the weight of a volume-calibrated pycnometer filled with a liquid of known density in which a certain quantity of the polymer sample²². Density of PMCHEMA was found as 1.18 g/cm³ by pycnometric measurement. The monomer and copolymer were characterized by using Mattson FT-IR-1000 spectrometer and Varian ¹H-and ¹³C-NMR spectra (200 MHz) at 25°C with CDCl₃ as solvent.

The FT-IR spectrum of the copolymer was the same as the characteristic peaks of the monomeric units. The stretch vibration bands of C=O group were observed for ester and acid in 1738 cm⁻¹. The stretching vibration band of -COOH was observed in 3500-2850 cm⁻¹ at acid units (broad). The ¹H-NMR spectrum of the copolymer showed peaks at 6.8-7.3 ppm, revealing the phenyl ring protons of PCHEMA units as a double. The signals at 4.2-3.1 ppm are assigned to -OCH₂-CH(OH)- for PCHEMA units. The signals at 1.2-2.0 ppm are due to -CH₃ of the cyclobutane ring and -CH₂-CH- and -CH₃ protons on the
copolymers. The signals of cyclobutane ring protons are at 2.2-2.9 ppm on the copolymer. The signal of -OH proton in methacrylic acid unit was shown at 11.5 ppm as singlet.

Instrumentation and procedure

A Shimadzu GC-14B model gas chromatography equipped with a dual flame ionization detector was used in the analysis. Dried nitrogen gas (research grade) was used as a carrier gas. Methane was used as a noninteracting marker to correct for dead volume in the column. The net retention time was determined from the positions of the peak maxima for methane and for the probe molecule at each temperature. Pressures at the inlet of the column, read from a mercury manometer, were used to compute corrected retention volumes by the usual procedures. Flow rates were measured from the end of the column with a soap bubble flow meter. A flow rate of about 20 ml min$^{-1}$ was used throughout our experiment. Spiral glass (3.2 mm I.D. $\times$ 1.1 m.) tubing was washed with methylene chloride and was annealed prior to use. A column of packing material was prepared by coating 60-80 mesh size Chromosorb W (DMCS) treated with PPCHEMA-co-MA. Then, 0.1415 g of PPCHEMA-co-MA was dissolved in 25 ml of tetrahydrofurane and 2.6308 g of the solid supporting materials were added to this solution and stirred. The solvent was removed by continuous stirring and slow evaporation under partial vacuum in a rotary evaporator. The prepared material was packed into a spiral glass tubing$^{14}$. The column was conditioned at a temperature above the glass transition temperature and at the fast carrier gas ($N_2$) flow rate for 24 h prior to use. The probes were injected onto the column with 1$\mu$L Hamilton syringes. Three consecutive injections were made for each probe during each set of measurements. An injection volume of 0.2$\mu$L was selected. The retention times of the probes were measured by using a Shimadzu CR6A Chromatopac model integrator. Methane was synthesized in the laboratory by the reaction of sodium acetate with sodium hydroxide$^{23}$.

Results and Discussion

The specific retention volumes, $V_g^o$, of 10 probes were obtained by using one loading PPCHEMA-co-MA at a series of temperatures (150, 160, 170 and 180°C). The values of specific retention volumes, $V_g^o$, of these probes were calculated according to equation (1) and are given in Table 1. As it is shown in Table 1, $V_g^o$, values changed for each group solvents with temperature. That is, the specific retention volumes, $V_g^o$, of the probes decreased with increasing temperature for each group of solvents.
Table 1. Variation of specific retention volumes, $V_g^\circ$ (ml/g), of some alcohols, ketones, acetates, aromatics and n-dodecane with temperature using poly [2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate-co-methacrylic acid] as stationary phase.

<table>
<thead>
<tr>
<th>Probe/T(°C)</th>
<th>150</th>
<th>160</th>
<th>170</th>
<th>180</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>6.73</td>
<td>6.52</td>
<td>6.01</td>
<td>5.76</td>
</tr>
<tr>
<td>Ethanol</td>
<td>6.98</td>
<td>6.65</td>
<td>6.06</td>
<td>6.10</td>
</tr>
<tr>
<td>Acetone</td>
<td>6.88</td>
<td>6.19</td>
<td>6.45</td>
<td>6.39</td>
</tr>
<tr>
<td>Ethyl methyl ketone</td>
<td>8.94</td>
<td>7.44</td>
<td>6.98</td>
<td>6.73</td>
</tr>
<tr>
<td>Methyl Acetate</td>
<td>8.80</td>
<td>6.42</td>
<td>6.06</td>
<td>5.89</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>9.00</td>
<td>7.57</td>
<td>6.93</td>
<td>6.81</td>
</tr>
<tr>
<td>Benzene</td>
<td>13.37</td>
<td>12.30</td>
<td>7.24</td>
<td>6.73</td>
</tr>
<tr>
<td>Toluene</td>
<td>16.21</td>
<td>15.14</td>
<td>13.61</td>
<td>11.25</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>40.51</td>
<td>35.93</td>
<td>32.17</td>
<td>26.08</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>82.27</td>
<td>73.96</td>
<td>58.77</td>
<td>44.50</td>
</tr>
</tbody>
</table>

The values for $\Omega_1^\infty$ and $\chi_1^\infty$ obtained using equations (2) and (7), respectively, are also shown in Table 2. The $\Delta H_1^\infty$ values of the probes were found from the slope of straight lines in Fig. 1. The partial molar free energy of mixing $\Delta G_1^\infty$ and the partial molar heats of mixing at infinite dilution of the solutes, $\Delta H_1^\infty$ calculated from equations (3) and (4) are shown in Table 3. The $\Delta H_1^\infty$ values of alcohols, ketones, acetates, and aromatics ranged from 6.36 to 7.10 kcal/mol, from 2.50 to 6.55 kcal/mol, and from 3.02 to 3.78 kcal/mol, respectively (Table 3). The $\Delta H_1^\infty$ value for n-dodecane was found to be 4.37 kcal/mol.

Table 2. Weight fraction activity coefficients, $\Omega_1^\infty$ and interaction parameters, $\chi_1^\infty$ of poly [2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethyl methacrylate-co-methacrylic acid] with some alcohols, ketones, acetates, aromatics and n-dodecane systems.

<table>
<thead>
<tr>
<th>Probe/T(°C)</th>
<th>150</th>
<th>160</th>
<th>170</th>
<th>180</th>
<th>$170^*$</th>
<th>150</th>
<th>160</th>
<th>170</th>
<th>180</th>
<th>$170^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>7.62</td>
<td>6.29</td>
<td>5.51</td>
<td>4.67</td>
<td>6.98</td>
<td>0.689</td>
<td>0.479</td>
<td>0.331</td>
<td>0.144</td>
<td>0.523</td>
</tr>
<tr>
<td>Ethanol</td>
<td>7.06</td>
<td>5.81</td>
<td>4.96</td>
<td>3.82</td>
<td>5.95</td>
<td>0.577</td>
<td>0.367</td>
<td>0.192</td>
<td>-0.096</td>
<td>0.485</td>
</tr>
<tr>
<td>Acetone</td>
<td>5.17</td>
<td>4.74</td>
<td>3.86</td>
<td>3.34</td>
<td>4.70</td>
<td>0.329</td>
<td>0.227</td>
<td>-0.004</td>
<td>-0.178</td>
<td>0.154</td>
</tr>
<tr>
<td>Ethyl methyl ketone</td>
<td>5.39</td>
<td>5.22</td>
<td>4.92</td>
<td>4.39</td>
<td>5.03</td>
<td>0.446</td>
<td>0.381</td>
<td>0.253</td>
<td>0.089</td>
<td>0.193</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>3.70</td>
<td>3.26</td>
<td>3.35</td>
<td>2.96</td>
<td>3.80</td>
<td>0.076</td>
<td>-0.044</td>
<td>-0.148</td>
<td>-0.201</td>
<td>0.036</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>4.42</td>
<td>4.29</td>
<td>3.91</td>
<td>3.37</td>
<td>4.30</td>
<td>0.238</td>
<td>0.196</td>
<td>0.088</td>
<td>-0.088</td>
<td>0.139</td>
</tr>
<tr>
<td>Benzene</td>
<td>4.91</td>
<td>4.36</td>
<td>4.05</td>
<td>3.88</td>
<td>6.09</td>
<td>0.508</td>
<td>0.367</td>
<td>0.319</td>
<td>0.190</td>
<td>0.478</td>
</tr>
<tr>
<td>Toluene</td>
<td>5.63</td>
<td>4.86</td>
<td>4.36</td>
<td>4.26</td>
<td>6.62</td>
<td>0.468</td>
<td>0.315</td>
<td>0.199</td>
<td>0.166</td>
<td>0.575</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>4.55</td>
<td>4.02</td>
<td>3.58</td>
<td>3.53</td>
<td>8.42</td>
<td>0.233</td>
<td>0.088</td>
<td>-0.037</td>
<td>-0.060</td>
<td>0.781</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>10.76</td>
<td>8.53</td>
<td>7.88</td>
<td>7.72</td>
<td>21.60</td>
<td>0.990</td>
<td>0.748</td>
<td>0.661</td>
<td>0.632</td>
<td>1.622</td>
</tr>
</tbody>
</table>

*References 26

It has been proposed that values for $\Omega_1^\infty$ greater than 5 are indicative of poor polymer-solute systems, while lower values indicate good solubility for such a system. Values for $\chi_1^\infty$ greater than 0.5 represent unfavourable polymer-solvent interactions, while values lower than 0.5 indicate favourable interactions in dilute polymer solutions. It will be seen that these values (in Table 2) according to $\Omega_1^\infty$ and $\chi_1^\infty$, acetates, aromatics, alcohols and ketones are good solvents, but that n-dodecane is non-solvent for PPCHEMA-co-MA. The interaction parameters, $\chi_1^\infty$, the partial molar free energy of mixing, $\Delta G_1^\infty$, the weight fraction activity coefficients, $\Omega_1^\infty$, and the partial molar heats of mixing at infinite dilution of the solutes, $\Delta H_1^\infty$, were
dependent on the number of carbons in the series (except alcohols). That is, these values \( \chi_{12}^\infty, \Omega_1^\infty \), \( \Delta G_1^\infty \) and \( \Delta H_1^\infty \) increased with increasing in the number of carbons in the series. But, in all series, \( \chi_{12}^\infty, \Omega_1^\infty \) and \( \Delta G_1^\infty \) the values decreased with increasing the column temperature.

Table 3. The partial molar free energies of mixing, \( \Delta G_1^\infty \) (kcal/mole), and partial molar enthalpy, \( \Delta H_1^\infty \), (kcal/mole) of poly [2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate-co-methacrylic acid] with some alcohols, ketones, acetates, aromatics and n-dodecane systems at 150-180°C.

<table>
<thead>
<tr>
<th>Probe/T((^\circ)C)</th>
<th>( \Delta G_1^\infty ) (kcal/mole)</th>
<th>( \Delta H_1^\infty ) (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>150</td>
<td>160</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.71</td>
<td>1.58</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.64</td>
<td>1.51</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.38</td>
<td>1.34</td>
</tr>
<tr>
<td>Ethyl methyl ketone</td>
<td>1.42</td>
<td>1.42</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>1.10</td>
<td>1.02</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>1.25</td>
<td>1.25</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.34</td>
<td>1.27</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.45</td>
<td>1.36</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>1.27</td>
<td>1.20</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>2.00</td>
<td>1.84</td>
</tr>
</tbody>
</table>

Figure 1. Variation of logarithm of weight fraction activity coefficients, \( \Omega_1^\infty \), with reciprocal of absolute column temperature, 1/T(K\(^{-1}\)) for poly [2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate-co-methacrylic acid] and some solutes: ◊: methanol, ♦: ethanol, ○: acetone, ⊗: EMK., ∆: methyl acetate, □: ethyl acetate, ○: benzene, ▽: toluene, ■: o-xylene, ×: n-dodecane

It may be seen from \( \chi_{12}^\infty \) and \( \Omega_1^\infty \) values that aromatics and alcohols are poor solvents for PPCHEMA\(^\text{26}\) (homopolymer) (see Table 2). In contrast, they are good solvents for PPCHEMA-co-MA (co-polymer) at 170°C.
Determination of the Thermodynamic Properties of Poly..., İ. KAYA, K. DEMİRELLİ

Figure 2. Variation of the term \([\delta_1^2/RT - \chi_{\infty}^1/V_1]\) with solubility parameters of the solutes, \(\delta_1\) (cal/cm\(^3\))\(^{0.5}\), at temperatures (a) = 170°C (b) = 180°C

Table 4. The solubility parameter, \(\delta_2\) (cal/cm\(^3\))\(^{0.5}\), of poly [2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate-co-methacrylic acid] at 170 and 180°C.

<table>
<thead>
<tr>
<th>(T(\text{°C}))</th>
<th>slope</th>
<th>intercept</th>
<th>from slope, (\delta_2)</th>
<th>from intercept, (\delta_2)</th>
<th>(r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>170</td>
<td>0.0158</td>
<td>-0.0547</td>
<td>6.95</td>
<td>6.94</td>
<td>0.9964</td>
</tr>
<tr>
<td>180</td>
<td>0.0152</td>
<td>-0.0515</td>
<td>6.84</td>
<td>6.81</td>
<td>0.9922</td>
</tr>
</tbody>
</table>

The solubility parameter of a polymer, \(\delta_2\), can be determined by equation (9)\(^9,16\). The solubility parameter \(\delta_2\) is determined from either the slope or the intercept of a straight line obtained by plotting the left-hand side of equation (9) versus \(\delta_1\). The solubility parameter of PPCHEMA-co-MA was evaluated from either the slope or the intercept of Fig. 2 as 6.95 (cal/cm\(^3\))\(^{0.5}\) or 6.94 (cal/cm\(^3\))\(^{0.5}\), respectively, at 170°C. The values of the solubility parameters of PPCHEMA-co-MA, \(\delta_2\), decreased with increasing temperature (see Table 4). Kaya et al.\(^{22,26}\) and Yilmaz et al.\(^{27}\) have determined the solubility parameters, \(\delta_2\), of poly methyl methacrylate (PMMA), poly (ethyl methacrylate) (PEMA), poly[2-(3-phenylcyclobutyl)-2-hydroxyethylmethacrylate] (PPCHEMA) and poly (p-chlorostyrene) to be 6.85 (cal/cm\(^3\))\(^{0.5}\), 5.99 (cal/cm\(^3\))\(^{0.5}\), 6.92 (cal/cm\(^3\))\(^{0.5}\) and 7.90 (cal/cm\(^3\))\(^{0.5}\) by equation (9) at 180°C and 162°C, respectively.

References

Determination of the Thermodynamic Properties of Poly..., İ. KAYA, K. DEMİRELLİ