Binding of Methyl Orange or Ethyl Orange Dyes by Some Dioxolane Copolymers: Synthesis of the Copolymers and Thermodynamics of the Dye–Copolymer Interactions

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Abstract: The extent of binding of methyl orange or ethyl orange by (2-phenyl-1,3-dioxolane-4-yl) methyl methacrylate (PDMMA), 2-hydroxyethyl methacrylate (HEMA), and vinyl-pyrrolidone (VPy) copolymers has been investigated by the equilibrium dialysis method. The dialysis experiments have been carried out in a Tris (hydroxy methyl) aminomethane buffer (pH = 7) and at the temperatures of 15, 25, and 35°C. The PDMMA-*co*-HEMA and PDMMA-*co*-VPy copolymers have been prepared in the laboratory by using the related monomers in different ratios. The synthesized products were analyzed by Fourier Transform-infrared spectroscopy (FTIR), proton nuclear magnetic resonance (^{1}H NMR) spectroscopy, differential thermal analysis (DTA), and differential scanning calorimetry (DSC) techniques. The binding extent of the dyes by the copolymers was determined by ultraviolet (UV) absorbance measurements. The results indicate that the extent of binding is relatively higher for ethyl orange than that for methyl orange under identical conditions. The binding slightly decrease with increasing temperature, and it is accompanied with favorable free energy, and exothermic enthalpy change within the temperature range studied. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3355–3361, 2004

Keywords: equilibrium dialysis; thermodynamics; 1,3-dioxalane; dye-binding

INTRODUCTION

Water-soluble synthetic polymers containing suitable apolar and ionic side chains exhibit strong affinities to bind small molecules.[1–5] Stochiometric or energetic characteristics of the binding interactions were examined particularly by the equilibrium dialysis method.[2,6–9] The earlier studies show, in general, that both apolar and ionic interactions contribute to the binding process, but temperature and pH of the medium also closely affect the extent of binding. Several experimental data, available in the literature, indicate that the binding of methyl orange by macromolecules is maximum around pH ~ 7–8. The temperature dependence of the binding is generally regular in the range of 5–35°C, and the extent of binding decreases with increasing temperature.[3,4] On the other hand, the temperature dependence of the binding of the relatively larger molecules, such as propyl orange or butyl orange, may not be regular. The literature data indicate that, if the enthalpy of the interactions is exothermic at a temperature while it is endothermic at other temperatures, the temperature dependence of the binding is not regular. Such situations are generally observed when both or either of the binding entities are sufficiently hydrophobic, and strong interactions are involved in the binding process.[7,10]

In this article, the synthesis and characterization of some of PDMMA-*co*-HEMA and PDMMA-*co*-VPy copolymers has been discussed in brief. In addition, the extent of the binding of methyl orange or ethyl orange by these copolymers has been investigated by the equilibrium dialysis method. The thermodynamic parameters related to the binding process and the changes in the binding energies depending on the copolymer type have also been discussed.

EXPERIMENTAL

Materials

Most of the materials and reagents used were of analytical grades and used as received. The molecular weight cutoff for the dialysis membrane used was 12,000. Methyl orange and ethyl orange were recrystallized from a water–ethanol mixture. Tris (hydroxy methyl) aminomethane solution (0.1 *M*) was used as the buffer at pH = 7.0. The HEMA was purified before use as a monomer because it contained ethylenglycol dimethyl methacrylate (EGDMA) and methacrylic acid (MA). The method of Montheard and Chappard[11] was adapted for the purification. The basic steps of the procedure applied for the purification is schematically represented in Figure 1.

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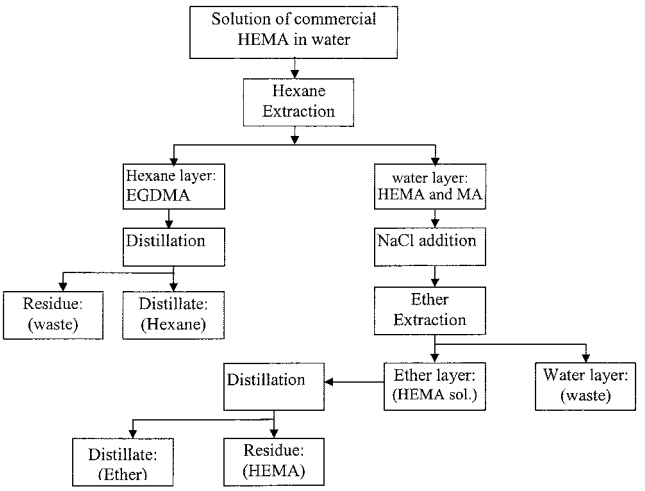

Figure 1 Schematic representation of the basic steps in the purification of commercial HEMA.

Synthesis of the monomers and copolymers

The monomer of PDMMA has been synthesized in the laboratory in two stages, as described in the literature.[12–16] In the first stage, 2-phenyl-5-hydroxy methyl-1,3-dioxolane was synthesized. A solution of 80 g (0.8 mol) benzaldehyde, 72.9 g glycerol (0.8 mol) and 4 *g* p-toluene sulfonic acid (PTS) in excess benzene (400 mL) was stirred overnight under the reflux conditions. The formed dioxolane was separated by successive extraction with benzene and ether, and then purified by a vacuum distillation. In the second stage, 15 g of the purified alcohol and 7 g of pyridine was dissolved in excess ether (300 mL) in a three-necked flask. The flask was inserted into an ice-water bath and methacroil chloride (9.6 mL) was then added dropwise over a period of 0.5 h. The mixture was stirred for an additional 24 h at room temperature to obtain PDMMA. The reaction scheme for the synthesis of PDMMA monomer is represented in Figure 2. The formed monomer was purified by the successive extractions, and then by distillation at 140°C, 1 mmHg.

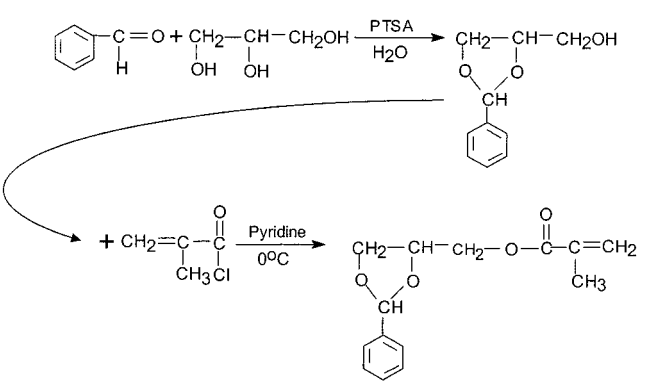

Figure 2 The reaction scheme for the preparation of the 1,3 dioxolane monomer.

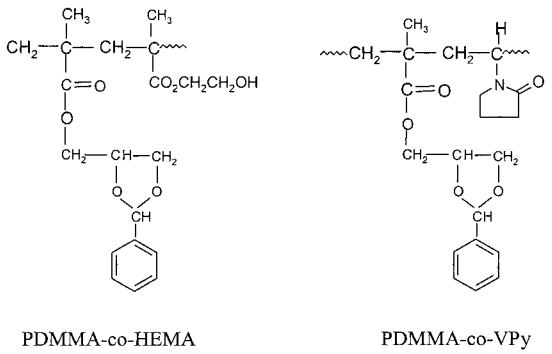

Figure 3 Structural characteristics of the PDMMA copolymers.

A method given in the literature[12–14,17] was adopted for the preparation of the homopolymer and the copolymers. For the HEMA homopolymer, the monomer and $\alpha\alpha'$-azoisobutyronitrile (AIBN) (0.2% of the monomer weight) in ethanol were mixed in a polymerization tube. The tube was purged with argon, sealed, and inserted into a water bath, and then allowed to react approximately for 1 h at 60°C. Then the tube was opened and poured into excess hexane to precipitate the polymer. The dissolution in ethanol and the precipitation in hexane were repeated two times, and then dried under vacuum at 40°C for 24 h. A similar procedure was applied in the preparation of the copolymers. For the copolymerization, an appropriate amount of the monomers and AIBN was dissolved in ethanol and reacted as described above. The copolymers were precipitated in excess ether. The monomers of the PDMMA, HEMA, and VPy were used in various proportions to prepare the copolymers with a different composition. The structural characteristics of the synthesized copolymers are represented in Figure 3.

Analysis of the products

The synthesized monomers and the copolymers were analyzed by ^{1}H NMR and FTIR spectroscopies, DTA, and DSC techniques. A Varian Gemini 200 MHz instrument was used in the ^{1}H NMR analysis. In the case of HEMA homopolymer, chloroform-*d*, in the case the copolymers, dimethyl sulfoxide-d_6 were used as the solvent and tetra methylsilane was used as the internal standard. The relative signal intensities of the spectra were measured from the integrated peak area. A Mattson 1000 Series FTIR spectrophotometer was used for IR analyses. A sample of about 1 mg was mixed with potassium bromide (KBr, 0.1 g) and pressed into a tablet form, dried under vacuum, and then the spectrum was recorded. A Shimadzu TGA-50 instrument was used for DTA analyses, and a Shimadzu DSC-50 instrument was used for the DSC analyses. The DTA

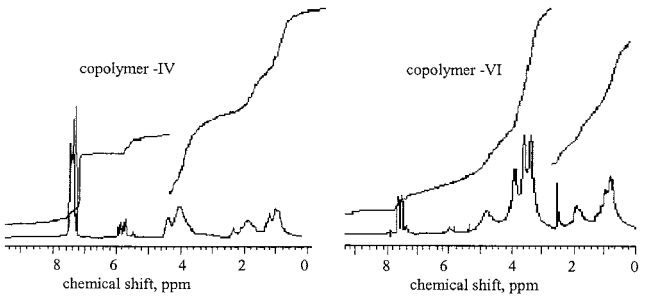

Figure 4 Typical ^{1}H NMR spectra for the two types of copolymers.

analyses were carried out in the range from ambient to 800°C with a heating rate of 20°C/min, DSC analyses were carried out in the range from ambient to 250°C with a heating rate of 20°C/min, under nitrogen atmosphere. α-Alumina was used as the reference material in the DTA and DSC analyses. A Shimadzu UV-2100 Series double-beam UV-VIS spectrometer was used for the determination of the dye concentrations at the equilibrium.

Equilibrium dialysis

The equilibrium dialysis experiments were carried out in a Tris (hydroxy methyl) aminomethane buffer (pH = 7) at the temperatures of 15, 25, and 35°C. At first, the concentrated stock solutions of the polymers and the dyes were prepared. The standard-absorbance plots were prepared by means of UV absorbance measurements of the standard solutions. In the dialysis experiments, a 10-mL aliquot of the polymer solution (0.06%) inside the dialysis bag was equilibrated with a 50 mL of the dye solution (in a concentration range of 1.5×10^{-4} *M*– 1.0×10^{-5} *M*) in a beaker. The solution outside the dialysis bag was continuously stirred by a magnetic stirrer. The dye concentrations were determined from absorbance measurements, according to the concentration–absorbance standard curve at their respective maximum absorption wavelengths. The dye concentration outside the dialysis bag did not change after 24 h; therefore, the equilibrium time was determined as 24 h. The dilution effect was taken into consideration in the determination of free dye concentration at the equilibrium.

RESULTS AND DISCUSSION

Spectroscopic analyses

Typical ^{1}H NMR spectra for the two types of the copolymers are presented in Figure 4. The NMR spectra of the both type of the copolymers showed peaks at 7.6–7.2 ppm (aromatic hydrogen), 6.0–5.4 ppm (hydrogen in —OCHO), 4.8–3.4 ppm [hydrogen in, —$COOCH_2CH(O)$— $CH_2(O)$], 2.2–1.6 ppm (hydrogen in —CCH_2—), 1.2–0.8 ppm (hydrogen in —CCH_3).[13–17] Based on the NMR analysis, the monomer ratios in the copolymers were also estimated. For this purpose, two approaches were applied. In the first, the estimations were based on the integrated peak intensities for the aromatic region and the aliphatic region. In the second, the integrated peak intensities that appear at approximately 4 ppm (corresponding to the protons in the —OCH_2) ester group in the methacrylate units) and the peak intensities at approximately 3.7 ppm (corresponding to the protons in the —CH_2—OH in HEMA) were compared.[18] Both approaches resulted in approximately the same monomer ratios. The monomer ratios used in the preparation of the copolymers, and the ratios estimated in the copolymers, are given in Table I. The data in the table indicate that PDMMA monomer is more reactive than HEMA monomer in the formation of PDMMA-*co*-HEMA copolymers. However, the situation is different in the case of PDMMA-*co*-VPy copolymer synthesis.

Typical IR spectra for each of the two type copolymers (PDMMA-*co*-HEMA and PDMMA-*co*-VPy) are presented in Figure 5. It is seen from the figure that the each type copolymers has characteristic adsorption bands at 750–690 cm^{-1} (monosubstitued benzene ring), at 1250–1050 cm^{-1} (—C—O—), at 1600–1625 cm^{-1} (—C=C—), 1720–1730 cm^{-1} (—COO—), 2850–

TABLE I
Comparisons of the Starting Monomer Ratios and the Estimated Monomer Ratios in the Synthesized Copolymers

Copolymer	Starting monomer ratio			Estimated PDMMA in copolymer ^{1}H-NMR	Estimated PDMMA in copolymer Fox equation
	PDMMA	HEMA	VPy		
Copolymer-I	10	90	—	15.2	19.0
Copolymer-II	20	80	—	23.5	—
Copolymer-III	30	70	—	37.2	—
Copolymer-IV	40	60	—	63.2	57.0
Copolymer-V	50	50	—	68.7	—
Copolymer-VI	30	—	70	7.6	—

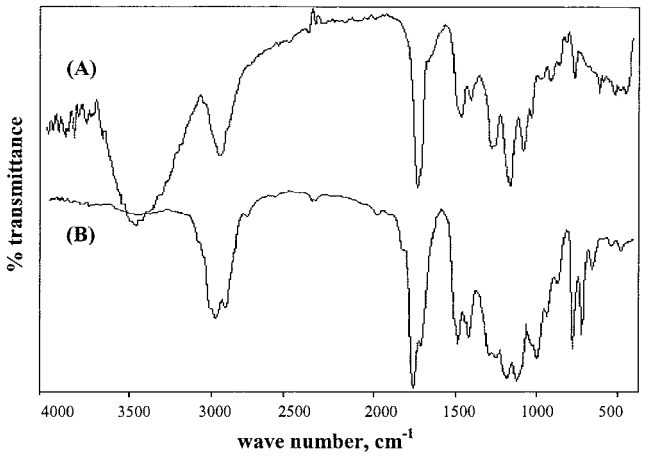

Figure 5 A comparison of the IR spectra of PDMMA-*co*-HEMA and PDMMA-*co*-VPy copolymers. (A) copolymer-I; (B) copolymer-VI.

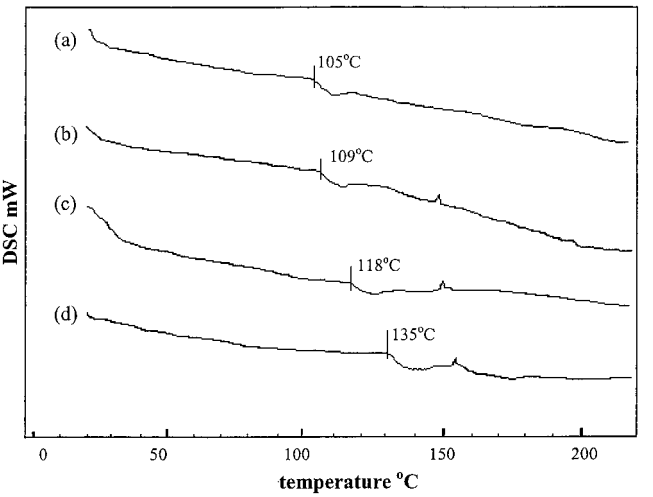

Figure 7 Typical DSC traces for the copolymer types. (a) HEMA homopolymer; (b) copolymer-I; (c) copolymer-IV; (d) copolymer-VI.

2950 cm^{-1} (aliphatic CH), 2900–3000 cm^{-1} (aromatic CH). In addition, the PDMMA-*co*-HEMA copolymer has strong and wide absorption around 3500 cm^{-1}, which is attributed to the OH of the alcohol structure. The PDMMA-*co*-VPy copolymer has a two-carbonil peak. In general, the IR spectra of the copolymers containing the same monomer showed a great similarity, as was expected.

Thermal characterization of the copolymers

Typical DTA traces for two copolymers are given in Figure 6. All of the PDMM-*co*-HEMA copolymers showed similar DTA traces, as represented in Figure 6(a). The figure indicates that there is a small endothermic peak in the traces of both the copolymers around 120–130°C. This peak may be related to the glassy transitions for the copolymers. There is another endothermic peak in the range of 240–300°C, depending on the type of the copolymer, which may be attributed to the starting of the melting. All of the PDMMA-*co*-HEMA copolymers showed a small exothermic peak around 350°C, but an intense exothermic peak starting at approximately 425°C. These observations suggest that these copolymers undergo a partial oxidation after 350°C. Starting of the oxidation for PDMMA-*co*-VPy is also around 350°C, and it is completed around 460°C. The DTA analyses also suggest that the PDMM-*co*-HEMA copolymers are thermally more stable than the PDMM-*co*-VPy copolymer.

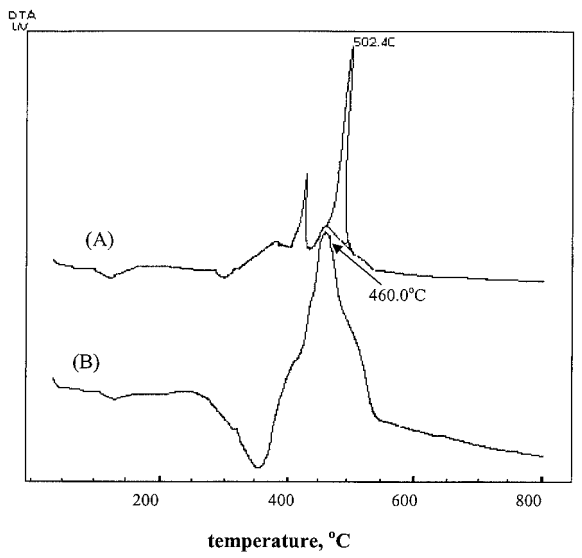

Figure 6 Typical DTA traces for the copolymer types. (A) Copolymer-I; (B) copolymer-II.

Glassy transition temperature (T_g) is the one the most important parameters that represents the molecular mobility of the polymer chains. Generally, DSC is used for the determination of T_g, and typical DSC traces of the copolymers are given in Figure 7. The figure indicates that T_g values vary, depending on the copolymer composition. Several approximations are given in the literature[18] to estimate T_g of a copolymer depending on the composition. For example, according to the Fox equation, T_g of a copolymer depends on the relative amount of each monomer and on the T_g of the respective pure homopolymer as follows:[18]

$$1/T_g = W_A/T_{g_A} + W_B/T_{g_B}$$

where T_g is the glass transition of a copolymer composed of two monomer units with the mass fractions W_A and W_B and the T_{g_A} and T_{g_B} are the glass transitions for the respective homopolymers. The reported T_g values for HEMA homopolymer and for PDMMA homopolymer in the literature are approximately 105

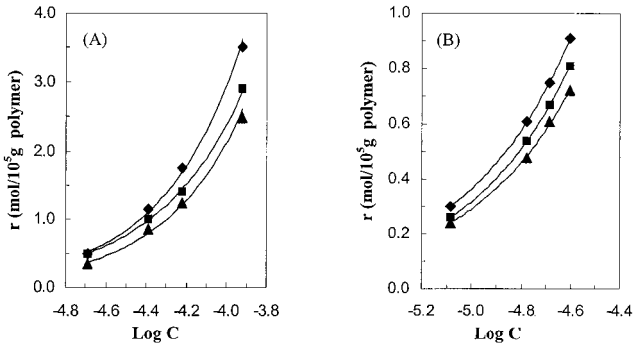

Figure 8 Extent of the binding of the dyes by copolymer I at various temperatures in 0.1 *M* Tris-acetate buffer of pH = 7. (A) Methyl orange; (B) methyl orange. ▲: 15°C,: ■: 25°C, ◆: 35°C.

and 130°C, respectively.[16] Based on these values and on the compositions given in Table I, the T_g values of the copolymers were estimated. The results indicated that the observed values and the estimated values from the Fox equation are in a good agreement. The results are also consistent with some of the values reported in the literature.[16,18]

Equilibrium dialysis data

The HEMA homopolymer and three different PDMMA-*co*-HEMA copolymers have been examined for their capacity to bind methyl or ethyl orange at three temperatures. Based on the standard–absorbance relation, a smaller concentration was chosen for ethyl orange experiments. The results indicate that the amount of bound-dye increases with increasing dye concentration but slightly decrease with the increasing temperature. A typical relation for the extent of binding of methyl orange and ethyl orange by copolymer-I is illustrated in Figure 8. The *r* values in the figure refer to the number of moles of the dye bound per 10^5 g of the polymer, and C refers to the free dye concentration at the equilibrium. Similar plots are obtained for the other copolymers. The data in the figures indicate that temperature has a relatively minor effect on the amount of bound dye (*r* value) in the range of 15–35°C. The *r* values are higher for ethyl orange than that for methyl orange under identical conditions. In addition, the data indicate that dye-adsorption capacity of the copolymers increase with increasing HEMA ratio in the copolymers. These observations suggest that the hydroxyl groups in the copolymers offer a site for the dye attachment.

Thermodynamic analysis

Thermodynamic parameters are important to understand the interactions between small molecules and macromolecules. Many investigations have been carried out to elucidate the energetic characteristics of these interactions and the binding of small molecules by macromolecules.[2,7,10,19] The relationship between the amount of bound-dye and the binding constant is generally evaluated from the double reciprocal plots for the bound-dye vs free dye, i.e., the Klotz plot of $1/r$ vs $1/C$, as follows:[2,5,10]

$$\frac{1}{r} = \frac{1}{nkC} + \frac{1}{n} \tag{1}$$

where *k* refers to the intrinsic binding constant, *n* is the number of the binding sites per 10^5 g of the polymer. The first binding constant *K* is defined as $K = nk$, and it is generally used for the quantitative comparison of the binding capacities of the macromolecules. The binding constant, as is seen from eq. (1), may be evaluated from the slope of the double reciprocal plots. Such plots are given in Figure 9 for the binding of methyl orange or ethyl orange by copolymer-I. Similar plots are obtained for the other copolymers. It may be seen from the figures that the intercept of these lines are very near to zero, suggesting that the *n* values are very large. A small error in estimation of the intercepts $(1/n)$ results in a large error in estimation of *n*. Therefore, it is more convenient to deal with *K* values and omit *k* and *n* values. Because almost straight lines are obtained by the Klotz plot, then the *K* values may be estimated from the reciprocal of the slopes. The estimated *K* values from the slopes are given in Table II.

The free enthalpy change of the binding is estimated from the binding constants:

$$\Delta G = -RT \ln K \tag{2}$$

The estimated ΔG values in this way are also given in Table II. The reaction enthalpy (ΔH) of the binding is estimated by means of the slope of the plots of ln*K*

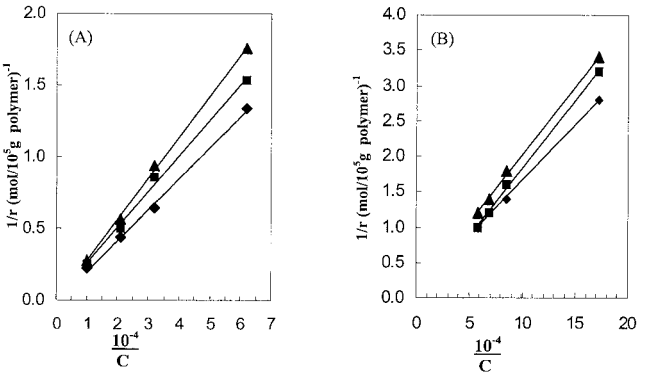

Figure 9 Relationship between $1/r$ and $1/C$ for the binding of the dyes by copolymer-I. (A) methyl orange; (B) methyl orange. ▲: 15°C,: ■: 25°C, ◆: 35°C.

TABLE II
The First Binding Constants and Thermodynamic Parameters for the Binding of Methyl Orange and Ethyl Orange by the Copolymers

	Methyl orange			Ethyl orange		
Parameter	15°C	25°C	35°C	15°C	25°C	35°C
Copolymer-I						
K^*10^{-4}	4.624	4.000	3.471	6.353	5.550	4.850
ΔG (cal)	−6147	−6274	−6398	−6329	−6468	−6603
ΔH (cal)	−2414	−2534	−2649	−2223	−2382	−2532
ΔS (e.u)	12.96	12.55	12.17	14.25	13.71	13.21
Copolymer-V						
K^*10^{-4}	2.733	2.318	1.890	4.456	4.050	3.660
ΔG (cal)	−5846	−5951	−6026	−6125	−6281	−6431
ΔH (cal)	−2335	−3279	−4163	−1516	−1740	−1950
ΔS (e.u)	12.19	8.97	6.05	16.00	15.24	14.55
Copolymer-VI						
K^*10^{-4}	4.456	3.784	3.333	4.999	4.460	3.860
ΔG (cal)	−6126	−6242	−6373	−6192	−6338	−6463
ΔH (cal)	−3033	−2544	−2088	−1589	−2301	−2968
ΔS (e.u)	10.74	12.41	13.91	15.97	13.54	11.34
HEMA homopolymer						
K^*10^{-4}	2.090	1.631	1.235	3.630	3.010	2.520
ΔG (cal)	−5692	−5743	−5765	−6008	−6106	−6202
ΔH (cal)	−3791	−4663	−5478	−3169	−3217	−3262
ΔS (e.u)	6.60	3.62	1.93	9.86	9.69	9.54

vs. $1/T$ (Van't Hoff plot). Such a plot for the investigated copolymers is given in Figure 10. The enthalpies (ΔH) are estimated from the plots of $\ln K$ vs $1/T$ as following:[3]

$$\Delta H = -R\left[\frac{d\ln K}{d(1/T)}\right] \quad (3)$$

Using the free enthalpy (ΔG) and the reaction enthalpy (ΔH), the entropy of binding (ΔS) is estimated as:

$$\Delta S = (\Delta H - \Delta G)/T \quad (4)$$

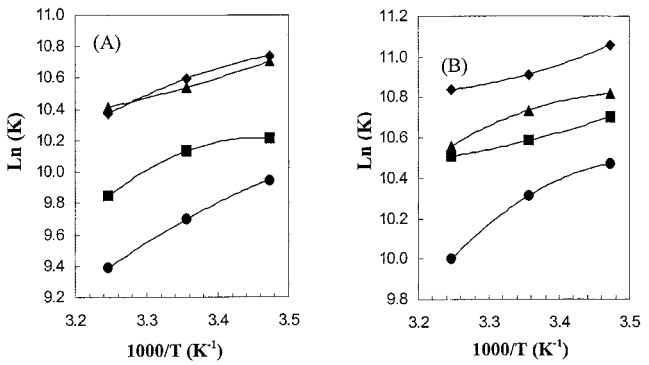

Figure 10 Relationship between $\ln K$ and reciprocal absolute temperature and $1/C$ for various copolymers. (A) Methyl orange; (B) methyl orange. ◆: copolymer-I, ●: copolymer-V, ▲: copolymer-VI, ■: HEMA homopolymer.

The estimated ΔH and ΔS values are also given in Table II. The data in the table indicate that the free energies (ΔG) are negative, which imply the binding of the dyes by the polymers are favorable. The ΔG values for ethyl orange are generally more negative (more favorable) than that for methyl orange in the binding by the same copolymer. The binding process is exothermic, and accompanied by a positive entropy change for all the cases investigated here. The enthalpy changes for the binding of methyl or ethyl orange is generally similar, but the entropy changes are considerably higher for ethyl orange than that for methyl orange. This suggests that the entropy change, during the formation of the dye–copolymer complex, more favorable for the binding. This result is in accord with the earlier observations given in the literature.[2,7,10]

CONCLUSIONS

The results indicate that PDMMA monomer show appreciably higher reactivity in the formation of PDMMA-*co*-HEMA copolymers. The glassy transition temperature of the copolymers varies in the range of 110–135°C, depending on the composition. The T_g values of the copolymers may be estimated from the compositional data and T_g values of the pure homopolymers.

The binding of methyl orange and ethyl orange by PDMMA-*co*-HEMA or by PDMMA-*co*-VPy copolymers is only slightly dependent on temperature within

the range studied. The bound-dye values are higher for ethyl orange than that for methyl orange under identical conditions. The dye binding capacity of the copolymers increase with increasing HEMA content in the copolymers. The homopolymer of HEMA exhibits the largest affinity for the dyes among the polymers investigated. This indicates the binding by HEMA is relatively stronger than that by PDMMA or VPy. These results suggest that increasing the hydrophobicity of the polymer result in an increase in the binding of the dyes. A favorable free energy of binding is accompanied by an entropy gain and exothermic enthalpy change. The entropy contribution to the free energy of the binding seems to be important.

References

1. Klotz, I. M.; Royer, G. P.; Sloniewsky, A. R. Biochemistry 1969, 12, 4752.
2. Takagishi, T.; Kuroki, N.; Naol, Y. J Polym Sci Polym Chem 1979, 17 1953.
3. Takagishi, T.; Kuroki, N. J Polym Sci Part A Polym Chem 1973, 11, 1889.
4. Takagishi, T.; Hosokawa, T.; Hatanaka, T. J Polym Sci Part A Polym Chem 1989, 27, 1.
5. Kozuka, H.; Hosokawa, T.; Takagishi, T. J Polym Sci Polym Chem 1989, 27, 555.
6. Shimizu, Y.; Kono, K.; Kim, I. S.; Takagishi, T. J Appl Polym Sci., 1995, 55, 255.
7. Kozuka, H.; Takagishi, T.; Hamano, H.; Kuroki, N J Polym Sci Part-A Polym Chem 1985, 23, 1243.
8. Yu, Y.; Zhuang, Y. Y.; Zou, Q. Chemosphere, 2001, 44, 1287.
9. Chattoraj, D. K.; Biswas, S. C.; Mahapatra, P. K.; Chatterjee, S. Biophysi Chemi 1999, 77, 9.
10. Takagishi, T.; Shibano, M. Polym Sci Part A Polym Chem 1987, 25, 2585.
11. Montheard, J.; Chappard, D., J. Macromol Chem Physi C 1992, 32, 1.
12. Pan, C. Y.; Wu, Z.; Bailey, W. J. J Polym Sci C Polym Lett 1987, 25, 243.
13. Coskun, M.; Ilter, Z. J Polym Sci A Polym Chem 2002, 40, 1184.
14. Ilter, Z.; Çoskun, M.; Erol, I. J Polym Sci Part A Polym Chem 2001, 39, 2326.
15. Ilter, Z.; Çoskun, M.; Erol, I.; Ünal, A.; Ahmetzade, M. Polym Degrad Stabil 2002, 75, 501.
16. Ilter, Z., PhD Thesis (in Turkish), Firat Univ., Elazig, 1997.
17. Takanori, T.; Uemura, A.; Ikada, N.; Motomura, K.; Aratona, M. J Physi Chem B 1998, 102, 3724.
18. Fernandez, M.; Fernandez-Garcia, G.; Torrado, M. F.; Martinez G. M.; Sanchez M. Polymer 2002, 41, 8001.
19. Saboury, A. A.; Sarri-Sarraf, N.; Saidian, S Themochim Acta 2002, 381, 147.