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ORIGINAL PAPER

Swelling of *N*-vinylcaprolactam–dodecyl methacrylate gel in {heptane + toluene} mixtures[‡]

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A copolymer gel has been synthesized from *N*-vinylcaprolactam and dodecyl methacrylate in ethanol using the free radical cross-linking polymerization method. Characterizations of the gel were performed by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and thermal gravimetric analysis (TGA) techniques. Swelling behavior of the gel was investigated in heptane, toluene, and their binary mixtures with different compositions. Swelling value in toluene is higher than that in heptane and swelling value increases with the increasing initial content of toluene in the binary mixture with heptane. The swelling values are correlated by the first- and second-order differential equations, and the best model correlating the experimental results is a second-order one. Diffusion coefficients have also been calculated for heptane and toluene at each concentration by power-law and first-order equations. While the diffusion mechanism of the gel in heptane is a Fickian one, the gel swelled in toluene exhibits a non-Fickian character. Diffusion mechanisms of the gels in binary mixtures are much more complicated. Because of the higher swelling degree in toluene compared to that in heptane, selectivity of the gel in different {heptane + toluene} mixtures with selectivity close to 1 has also been taken into consideration.

Keywords: *N*-vinylcaprolactam, dodecyl methacrylate, heptane, toluene, swelling kinetics, diffusion

Introduction

A gel is a cross-linked, three dimensional polymer network; cross-linking causes swelling of the gel instead of its dissolution in solvents. Swelling behavior of a gel can be affected by some parameters such as temperature (Imaz & Forcada, 2009; Zhang et al., 2001), pH (Zhou et al., 2003; Zhao et al., 2010) or ionic strength (Peng & Wu, 2001). Cross-linked polymers play an important role in chemical engineering research because of the wide range of chemical applications, e.g. separation, biomedical and biochemical applications, and oil absorption. Atta et al. (2005) synthesized oil-absorptive 1-octene and isodecyl acrylate copolymers including different cross-linkers such as ethylene glycol diacrylate and ethylene glycol dimethacrylate by both radical initiation and electron-beam irradiation techniques. They measured swelling properties of copolymers in toluene and petroleum crude oil and found that the highest oil absorbancy is provided by gels prepared by electron-beam irradiation. Atta et al. (2007) synthesized a copolymer of octadecene and maleic anhydride as a crude oil absorber. Ceylan et al. (2009) prepared a butyl rubber sorbent at three different temperatures namely at 17 °C, –2 °C, and –18 °C to remove polycyclic aromatic hydrocarbons from seawaters and concluded that butyl rubber prepared at –18 °C is an efficient material for oil spill cleanup and the removal of polycyclic aromatic hydrocarbons.

Literature includes many studies about swelling behavior of gels in aqueous solutions and solutions

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with different pH values, temperatures, etc., but scarcely in solvents or solvent mixtures (Park et al., 1999; Aşçi & Hasdemir, 2008; Ozmen & Okay, 2003; Caykara et al., 2006). Çakal and Çavuş (2010) prepared poly(*N*-vinylcaprolactam-*co*-2-(diethylamino) ethyl methacrylate) gels using cross-linkers, ethylene glycol dimethacrylate and allyl methacrylate, and their stimuli-sensitive behavior were studied by the authors. Çavuş and Çakal (2012) synthesized the poly(*N*-vinylcaprolactam-*co*-itaconic acid) gel in both ethanol and ethanol–water medium using the free radical cross-linking polymerization method at 60 ℃ for 24 h. They used azobis(isobutyronitrile) (AIBN) and allyl methacrylate (AMA) as the initiator and the crosslinking agent, respectively, and studied the stimuli-sensitive behavior of the prepared gels. The authors (Çakal & Çavuş, 2010; Çavuş & Çakal, 2012) emphasized the advantages of the amphiphilic structure of the *N*-vinylcaprolactam monomer. In the present study, a copolymer gel using *N*-vinylcaprolactam and dodecyl methacrylate (poly(*N*-vinylcaprolactam-*co*-dodecyl methacrylate, P(VC-co-DDMA)) was prepared and its swelling behavior in heptane, toluene, and binary mixtures of heptane and toluene were studied.

Separation of the {heptane + toluene} system was presented in literature using solvent extraction to obtain liquid–liquid equilibrium data. Solvents used to separate this system are sulfolan, γ-butyrolactone, benzyl alcohol, triethylene glycol, tetraethylene glycol, *N*-formylmorpholine, and *N*-methyl pyrrolidone (Ashcroft et al., 1982; Awwad et al., 1988; Sevgili, 2010; Hughes & Haoran, 1990; Saha et al., 1998; Letcher & Naicker, 1998). However, extraction of the {heptane + toluene} system by gel has not been presented in literature so far. In this study, because of higher swelling behavior of the gel in toluene than in heptane, the possibility of the separation of this mixture using the {*N*-vinyl caprolactam–dodecyl methacrylate} gel has been investigated. In this study, the separation efficiency has been characterized in terms of swelling values of each component of the gel and also of the selectivity of the gel.

Swelling values of the gel were determined gravimetrically, and were defined as "total swelling value" representing the total absorbed heptane and toluene amounts. On the other hand, swelling behavior of the gel was also calculated for each absorbed component using gas chromatography and mass balance.

Experimental

Materials and methods

N-vinylcaprolactam and triethylene glycol dimethacrylate (TEGDMA) were supplied by Aldrich (Steinheim, Germany) with purity of 98 % and by Fluka Chemie (Steinheim, Germany) with purity > 95 %. Dodecyl methacrylate (purity 60–70 %) was supplied by Merck (Schuchardt, Germany). Heptane, toluene, ethanol, and azobis(isobutyronitrile) (AIBN) were supplied by Merck (Darmstadt, Germany) with purity of 99 %, 99 %, 99 %, and 98 %, respectively. AIBN was recrystallized three times from methanol and dried under vacuum at 30 ℃. All other chemicals were used without any purification.

Poly(*N*-vinylcaprolactam-*co*-dodecyl methacrylate) (P(VC-co-DDMA)) gel was synthesized in ethanol by the free radical polymerization method. Polymerization of VC (2.5 g) and DDMA (2.87 mL) was performed at 60 ℃ for 24 h. AIBN (33.6 mg) and TEGDMA (55.2 µL) were used as the initiator and cross-linker, respectively. After passing of nitrogen from the {monomers + ethanol} mixture including TEGDMA for 20 min, the initiator was added to the solution and polymerization was carried out in glass tubes in a water bath (Polyscience, Niles, IL, USA) with a temperature controller. At the end of the reaction, glass tubes were broken and gels were sliced into small disks. Unreacted components were extracted from the gels by hot ethanol. Each extracted gel was dried in air and then under vacuum at 40 ℃ until a constant mass was reached.

Gels dried in a vacuum oven were grounded to powder. A mixture including 1 mass % of powdered sample and 99 mass % of FTIR grade KBr was pressed under the pressure of 20 MPa to make a pellet. FTIR bands were recorded by a Perkin–Elmer Precisely Spectrum One (Perkin–Elmer, Shelton, CT, USA) in the range of 450–4000 cm^{-1}.

Thermal characterization of dried gels was performed by simultaneous DTA-TGA apparatus Shimadzu DTG-60 (Shimadzu, Kyoto, Japan). Weighed samples (ca 10 mg) placed in a platinum pan were analyzed under nitrogen atmosphere and heating from 30 ℃ to 1000 ℃ at the rate of 10 ℃ min^{-1}.

Morphologic characterization of the gels was done on a SEM apparatus FEI-Quanta FEG 450, (Quanta, Hillsboro, OR, USA). The gels were immersed in a solvent/solvent mixture until the swelling equilibrium was reached and dried at room temperature. Dried gels were coated with gold before the SEM analysis.

All samples withdrawn from the solvent mixtures were analyzed by gas chromatography (Clarus 500) (Perkin–Elmer, Shelton, CT, USA) with the accuracy of ± 0.002 in terms of mass fraction. The analyses were performed using an FID detector and a Valco-Bond capillary column of 30 m × 320 µm × 1 µm. To analyze the samples, binary mixtures of {heptane + toluene} with different compositions were prepared and 0.1 mL of each mixture was mixed with 1.5 mL ethanol for calibration. Rainin SL-100 was used to withdraw a 0.1 mL sample with the accuracy of $\pm 8 \times 10^{-4}$ mL and Rainin SL-5000 was used to withdraw a 1.5 mL sample with the accuracy of $\pm 1.5 \times 10^{-4}$ mL. Optimum conditions of analysis are as follows: temperature of the injection block and detector of 523 K and 543 K, respectively; carrier gas: helium with the flow rate of 1 mL min^{-1}; split ratio of 75 : 1; oven temperature programmed from 323 K and increasing at the rate of 10 K min^{-1} to 423 K. Samples of each phase were analyzed at least two times, and the average values were used.

Determination of gel swelling properties and swelling kinetics

Swelling values (M_t) of the P(VC-co-DDMA) gel in heptane and toluene were determined gravimetrically as a function of time

$$M_t = \frac{W_\text{S} - W_\text{D}}{W_\text{D}} \tag{1}$$

where W_S and W_D are masses of swollen and dry gels, respectively.

Binary mixtures of heptane and toluene with toluene concentration of 20 mass %, 30 mass %, 50 mass %, and 70 mass % were also prepared to determine the swelling values of the gels in these mixtures. The values were determined gravimetrically using a Mettler–Toledo New Classic MS 204S (Mettler–Toledo, Columbus, OH, USA) with the accuracy within ± 10^{-7} kg and calculated using Eq. (1). Since these swelling values include those of the total absorbed components, the term “total swelling value” was used. However, since the gel absorbs both heptane and toluene at different diffusion rates, swelling values of the gel for each component in the mixture cannot be determined only gravimetrically. Instead, swelling values of each component were determined by analyzing the {heptane + toluene} mixture samples by GC, and calculating mass fraction and mass of each component in the mixture. Mass fraction of each component in the solvent mixture was calculated using concentration values taken from the GC analysis and the amount of each component in the solvent mixture was calculated as

$$m_{i,\text{s}} = m_\text{T} w_{i,\text{s}} \tag{2}$$

where $m_{i,\text{s}}$ is the amount of component i in the solvent mixture at time t, m_T is the amount of total solvent mixture determined gravimetrically, and $w_{i,\text{s}}$ is the mass fraction of component i in the solvent mixture.

Regardless of the amount of samples used for the analysis, the amount of component i absorbed by the gel was calculated by the following equation:

$$m_{i,\text{gel}} = m_{i,\text{s},0} - m_{i,\text{s}} \tag{3}$$

where $m_{i,\text{gel}}$ is the amount of component i absorbed by the gel at time t and $m_{i,\text{s},0}$ is the amount of component i in the solvent mixture at $t = 0$ s.

Finally, swelling values of the gel for each component were calculated using the total swelling value and the mass fraction of each component in the gel

$$M_{t,i} = M_t w_{i,\text{gel}} \tag{4}$$

where $M_{t,i}$ is the swelling value of the gel for component i and $w_{i,\text{gel}}$ is the mass fraction of component i in the gel.

Swelling kinetics of gels was investigated using the power law equation as well as the first- and second-order models.

Initial swelling data can be fitted to a power law equation (Chern et al., 2004; El-Hamshary, 2007; Karadağ et al., 2001; Cai & Gupta, 2001):

$$\frac{M_t}{M_\infty} = kt^n \tag{5}$$

where k is a characteristic constant of the gel, n is a kinetic constant for solvent transport into the gel, and M_∞ is the swelling value at equilibrium. So, the diffusion coefficient can be calculated from the following equation (Chern et al., 2004):

$$\frac{M_t}{M_\infty} = \frac{4}{L}\sqrt{\frac{Dt}{\pi}} \quad \text{for} \quad \frac{M_t}{M_\infty} \leq 0.6 \tag{6}$$

where D is the effective diffusion coefficient in the gel disk, and L is the thickness of the disk.

In the first-order model, the rate of swelling is directly proportional to the swelling capacity before reaching the equilibrium (Kim et al., 2003; Katime et al., 1996):

$$\frac{\text{d}M_t}{\text{d}t} = k_1 (M_\infty - M_t) \tag{7}$$

where k_1 is the first-order constant. The solution of this differential equation can be written as:

$$\ln\left(\frac{M_\infty}{M_\infty - M_t}\right) = k_1 t \tag{8}$$

The diffusion coefficient can be calculated using k_1. The Fick’s second law in terms of the swelling ratio can be written as:

$$\frac{\partial M_t}{\partial t} = D\frac{\partial^2 M_t}{\partial z^2} \quad \text{for} \quad -\frac{L}{2} < z < \frac{L}{2} \tag{9}$$

The initial (IC) and boundary (BC) conditions for the above equation are as follows:

$$\text{IC: at } t = 0 \text{ for } -L/2 < z < L/2 \; M_\text{t} = M_0 = 0 \tag{10}$$

$$\text{BC1: at } 0 < t < \infty \text{ for } z = \pm\, L/2 \; M_\text{t} = M_\infty \tag{11}$$

$$\text{BC2: at } t > 0 \text{ for } -L/2 < z < L/2 \; M_\text{t} = M_\text{t} \tag{12}$$

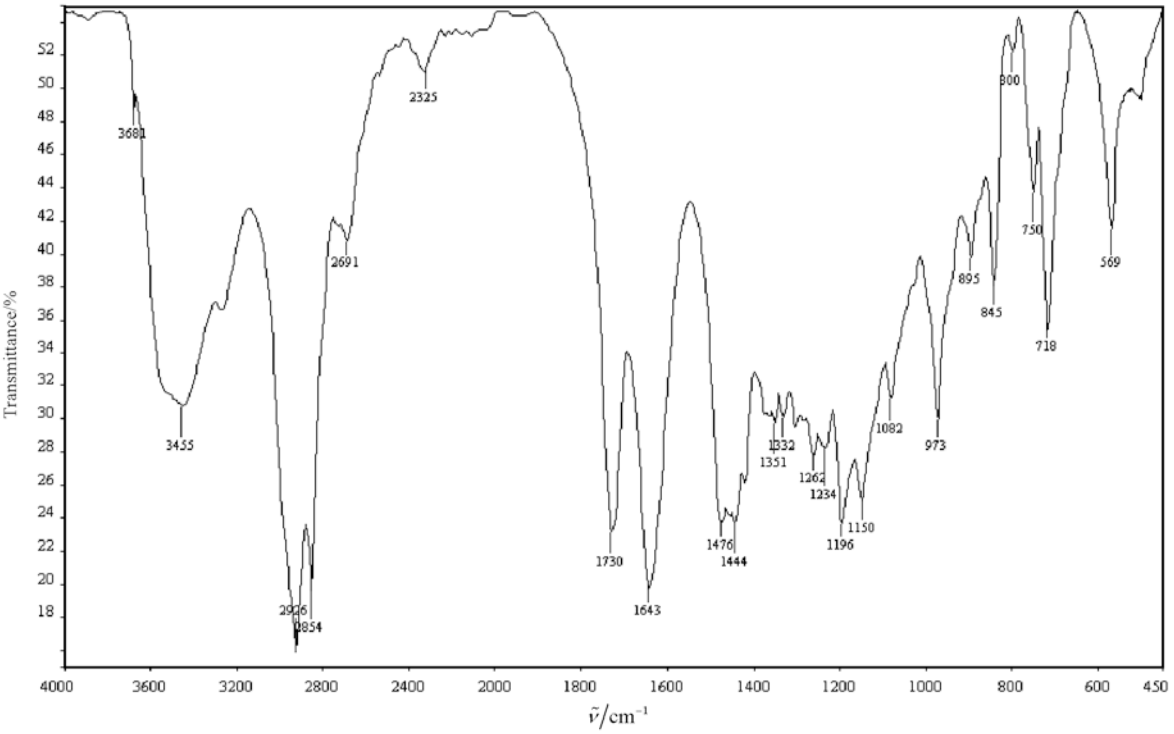

Fig. 1. FTIR spectrum of P(VC-co-DDMA).

The solution of this equation assuming constant values of D and L for the whole process is given as

$$\frac{M_\infty - M_t}{M_\infty - M_0} = \frac{M_\infty - M_t}{M_\infty} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left\{-\left[\frac{(2n+1)\,\pi}{L}\right]^2 Dt\right\} \quad (13)$$

For long swelling times, this equation is reduced to (Chern et al., 2004; Katime et al., 1996; Bellili et al., 2012):

$$\ln\left(\frac{M_\infty}{M_\infty - M_t}\right) \cong \frac{\pi^2 Dt}{L^2} \quad (14)$$

which is identical to Eq. (8) when $k_1 = \pi^2 D/L^2$. Thus it is possible to calculate diffusion coefficients of components from the value of k_1 assuming constant disk thickness and component/components absorption from the liquid phase.

In the second-order model, the swelling rate is defined as (Kim et al., 2003; Katime et al., 1996)

$$\frac{\mathrm{d}M_t}{\mathrm{d}t} = k_2\left(M_\infty - M_t\right)^2 \quad (15)$$

where k_2 is the second-order constant. Integration of Eq. (15) gives

$$\frac{t}{M_t} = \frac{1}{k_2 M_\infty^2} + \frac{t}{M_\infty} \quad (16)$$

Results and discussion

Gel characterization

FTIR spectrum of the P(VC-co-DDMA) copolymer gel is given in Fig. 1. The band at 1643 cm^{-1} shows the characteristic C=O (amide I) stretching vibration (Loos et al., 2003; Okhapkin et al., 2003; Qiu & Sukhishvili, 2006; Shtanko et al., 2003; Prabaharan et al., 2008). C=O stretching band can be observed at 1730 cm^{-1} due to the ester carbonyl of DDMA (Gürdağ, & Çavuş, 2006). Peaks at 1196 cm^{-1} and 1082 cm^{-1} are due to the C—N stretching (Usanmaz et al., 2009; Feng et al., 2009). The peak observed at 718 cm^{-1} is due to the polymethylene groups of DDMA (Shah et al., 2010; Çavuş, & Gürkaynak, 2006). *N*-vinylcaprolactam is the structural homologue of *N*-vinylpyrrolidone. Therefore, the bands at about 1422 cm^{-1}, 1444 cm^{-1}, and 1476 cm^{-1} (triplet) result from the characteristic vibrations of the lactam ring (Ekici, & Saraydın, 2007). Peaks observed at 2926 cm^{-1} and 2854 cm^{-1} were assigned to the asymmetric and symmetric C—H stretching vibrations, respectively (Prabaharan et al., 2008; Usanmaz et al., 2009; Feng et al., 2009).

Results of the TGA analysis of the P(VC-co-DDMA) copolymer gel is given in Fig. 2. Two evident degradation steps were observed. The sharp and broad weight decrease between 298–460 °C (mass loss: 84 %) can be assigned to the depolymerization (Usanmaz et al., 2009), followed by a narrow degradation step.

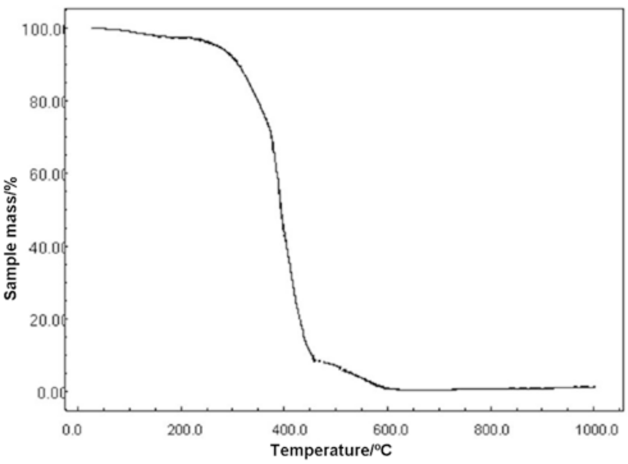

Fig. 2. TGA analysis of the P(VC-co-DDMA) gel.

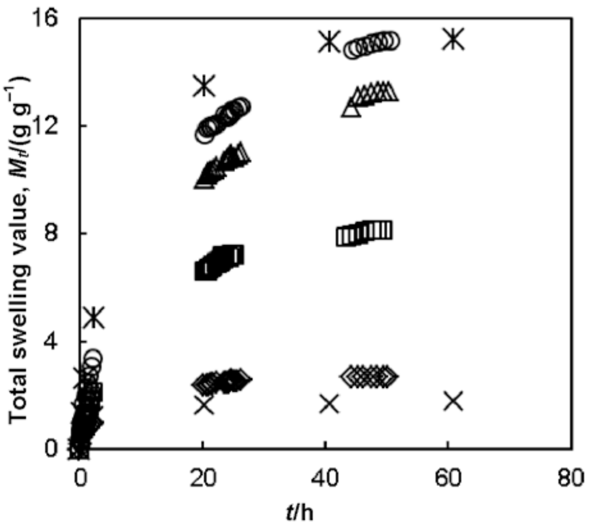

Fig. 3. Total swelling values of P(VC-co-DDMA) gels in heptane (×), toluene (∗), and {heptane + toluene} mixture with different toluene concentration/mass %: 20 (◇), 30 (□), 50 (△), and 70 (○).

Dynamic swelling behavior of P(VC-co-DDMA) gels

Dynamic swelling studies were performed to investigate the time-dependent swelling behavior of P(VC-co-DDMA). Fig. 3 shows the swelling values of P(VC-co-DDMA) gels in heptane, toluene, and their mixtures with toluene concentration of 20 mass %, 30 mass %, 50 mass %, and 70 mass %. These values are the total swelling values since they reflect the total absorbed amount of toluene and heptane in the mixtures. While the highest swelling value was obtained in toluene, the lowest swelling value was calculated for heptane. Increasing the concentration of toluene in a binary mixture also increased the total swelling values of the gel.

Swelling values of P(VC-co-DDMA) gels in heptane, toluene, and {heptane + toluene} mixtures

The effect of each component on the swelling behavior can be investigated by the calculation of heptane and toluene concentrations in the gel through a mass balance using the concentrations of each component in the liquid phase obtained by gas chromatography. Fig. 4 shows the swelling behavior of the P(VC-co-DDMA) gel for each component in the solvent mixtures with different toluene content.

As shown in Figs. 4a and 4b, equilibrium swelling values of the P(VC-co-DDMA) gel including that for heptane in mixtures with the initial toluene concentrations of 20 mass % and 30 mass %, respectively, are relatively higher. Swelling values in the mixture are defined as the amount of each component absorbed by the gel per dry mass. When the initial concentration of toluene in the mixture increases, the equilibrium swelling value for toluene also increases; on the other hand, the swelling value for heptane increases until the concentration of toluene reaches 50 mass % and the swelling values and equilibrium swelling values for heptane (component 1) and toluene (component 2) are similar (i.e., $M_{\infty,1} = 6.7$ g g^{-1} and $\mathrm{M}_{\infty,2} = 6.6$ g g^{-1}). Further increase in the initial toluene concentration causes a decrease in the swelling value for heptane and an increase in that value for toluene (Fig. 4c), which reflects the effect of the initial concentration of toluene on the swelling behavior of the gel.

Because of the swelling dynamics of the gel, the ability of the gel to separate {heptane + toluene} binary mixtures with respect to the initial concentration of toluene was also studied (Figs. 5 and 6). Fig. 5 shows how the fraction of toluene in the gel phase changes with the fraction of toluene in the solvent mixture. Although the swelling value of the gel in toluene is the highest and that in heptane is the lowest, selectivity of the gel is not higher than 1, which leads to the conclusion that separation cannot be achieved by the gel synthesized.

Diffusion coefficients of heptane and toluene were calculated from both Eqs. (6) and (14) and the values are given in Table 1.

Model parameters

Experimental swelling values were correlated by first- and second-order models defined by Eqs. (8) and (16), respectively. Root-mean square deviation (RMSD) values for each model were calculated using the following equation

$$\mathrm{RMSD} = \left[\sum_{i=1}^{N} \frac{(M_{t,\mathrm{exp}} - M_{t,\mathrm{model}})}{N} \right]^{0.5} \tag{17}$$

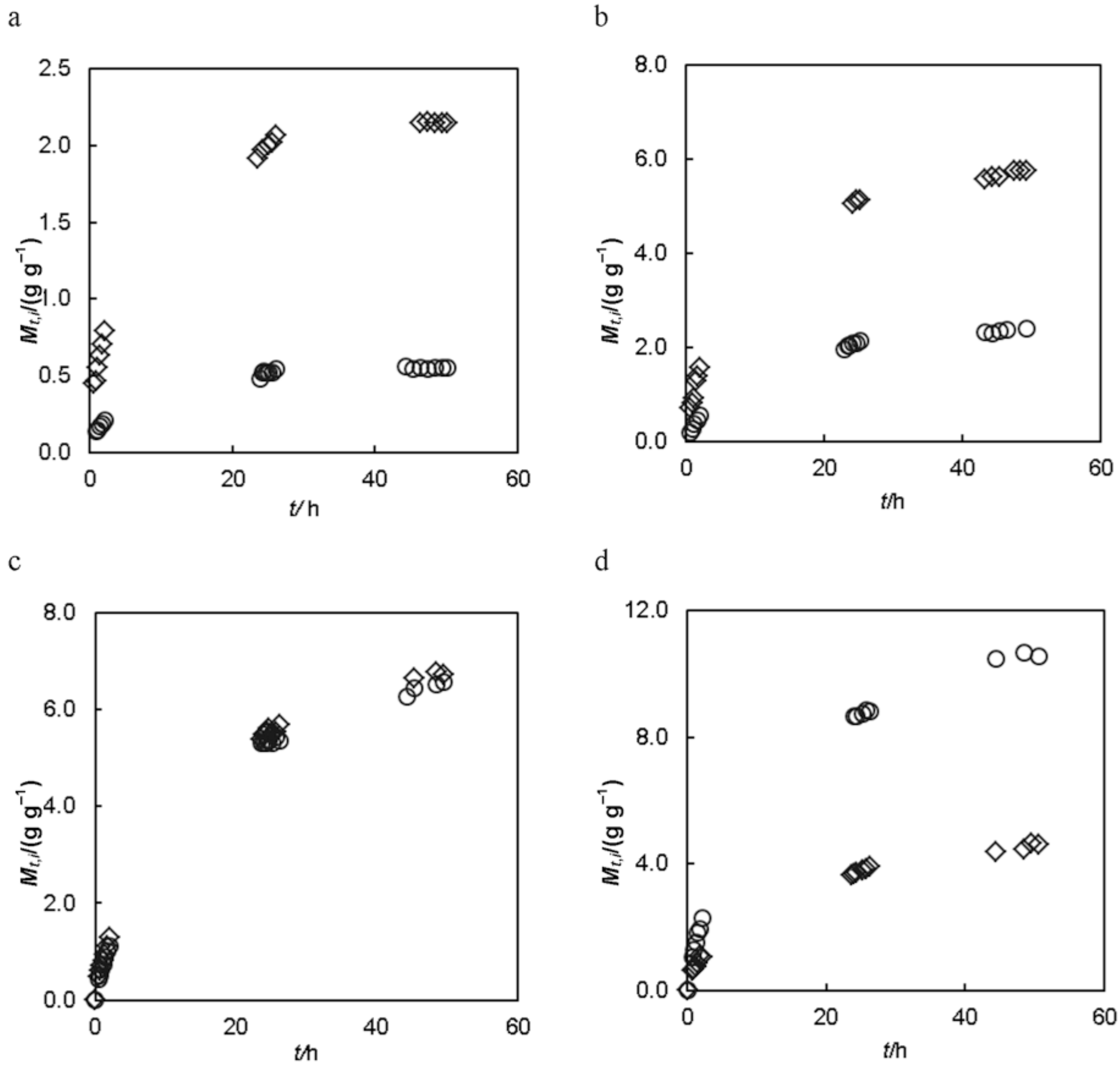

Fig. 4. Swelling behavior of the P(VC-co-DDMA) gel vs. time in the {heptane + toluene} mixture with toluene concentration/mass %: 20 (a), 30 (b), 50 (c), and 70 (d). Component swelling values computed for heptane (◇) and toluene (○).

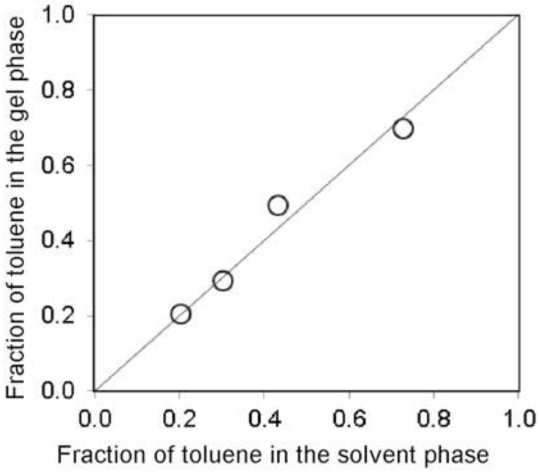

Fig. 5. Toluene fraction in the gel phase vs. toluene fraction in the solvent phase.

where N is the number of experiments, $M_{t,\mathrm{exp}}$ and $M_{t,\mathrm{model}}$ are the swelling values of the gel for heptane and toluene calculated from those obtained experimentally and by the model, respectively.

Parameters of these models for {heptane + toluene} mixtures with different toluene content are given in Table 2. Those of the first-order model are presented with sufficiently high regression values to achieve linear relationship of $\ln\left(\frac{M_\infty}{M_\infty - M_\mathrm{t}}\right)$ vs. time. In the second-order model with high regression values of t/M_t vs. time, the RMSD values are more suitable than those obtained by the first-order model to correlate the experimental swelling values.

Parameters of the power-law model are given in Table 3, Fickian diffusion mechanism was observed for the gel swollen in heptane and the non-Fickian for

Table 1. Diffusion coefficients of heptane (1) and toluene (2) and of each component in binary mixtures calculated from Eqs. (6) and (14)

Component/mixture	Eq. (6)		Eq. (14)	
	$D_1/(\mathrm{cm^2\ s^{-1}})$	$D_2/(\mathrm{cm^2\ s^{-1}})$	$D_1/(\mathrm{cm^2\ s^{-1}})$	$D_2/(\mathrm{cm^2\ s^{-1}})$
heptane (0 % toluene)	2.81×10^{-6}	–	3.86×10^{-7}	–
toluene (100 % toluene)	–	3.59×10^{-7}	–	5.22×10^{-7}
20 mass % of toluene	5.41×10^{-7}	5.94×10^{-7}	5.68×10^{-7}	4.73×10^{-7}
30 mass % of toluene	2.98×10^{-7}	1.99×10^{-7}	4.38×10^{-7}	4.53×10^{-7}
50 mass % of toluene	1.59×10^{-7}	1.34×10^{-7}	4.62×10^{-7}	4.45×10^{-7}
70 mass % of toluene	4.02×10^{-7}	2.92×10^{-7}	5.54×10^{-7}	6.57×10^{-7}

Table 2. Parameters of the models with RMSD values

	First-order model			Second-order model		
	k_1	R^2	RMSD	k_2	R^2	RMSD
in heptane	0.09	0.65	0.49	0.001	0.999	0.09
in toluene	0.12	0.99	0.81	0.24	0.998	0.49
20 mass % of toluene						
heptane	0.13	0.97	0.19	0.14	0.999	0.04
toluene	0.11	0.95	0.05	0.53	0.998	0.01
30 mass % of toluene						
heptane	0.086	0.99	0.36	0.03	0.999	0.06
toluene	0.089	0.96	0.08	0.06	0.999	0.10
50 mass % of toluene						
heptane	0.081	0.93	0.25	0.02	0.995	0.12
toluene	0.078	0.95	0.22	0.02	0.996	0.10
70 mass % of toluene						
heptane	0.070	0.99	0.30	0.03	0.994	0.15
toluene	0.083	0.93	0.48	0.01	0.996	0.30

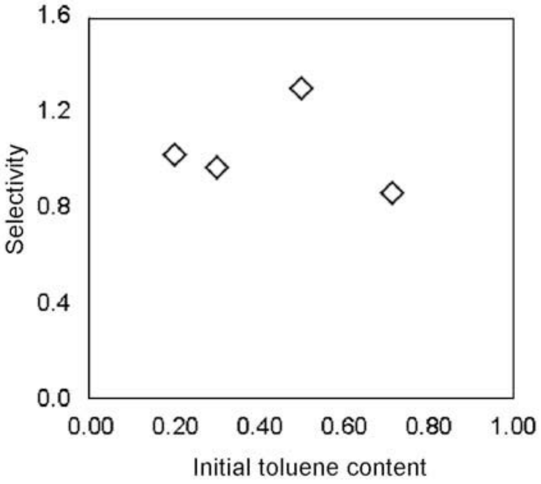

Fig. 6. Selectivity of the gel for toluene vs. the initial toluene concentration.

the gel swollen in toluene, which is also confirmed by higher swelling values achieved in toluene than in heptane. The value of n indicates that swelling is mainly a Fickian process for the gel in heptane where the polymer chain relaxation has little effect. In case of the gel in toluene, the polymer chain relaxation has a major effect on swelling. The diffusion mechanism is much more complicated in mixtures, i.e. Fickian diffusion mechanism for each component absorbed by the gel in the mixture with 20 mass % toluene was observed. On the other hand, each component in the mixtures with 30 mass %, 50 mass %, and 70 mass % of toluene causes non-Fickian behavior of the gel. Thus, Fickian behavior of the gel in each component of the mixture with relatively high concentration of heptane has been confirmed. Despite the Fickian behavior in heptane, an increase in the toluene concentration causes non-Fickian behavior of each component in the mixture. Interaction between toluene and heptane and the higher swelling ability of the gel in toluene may be responsible for this effect.

Morphology

Fig. 7 shows the SEM images of the cross-sections

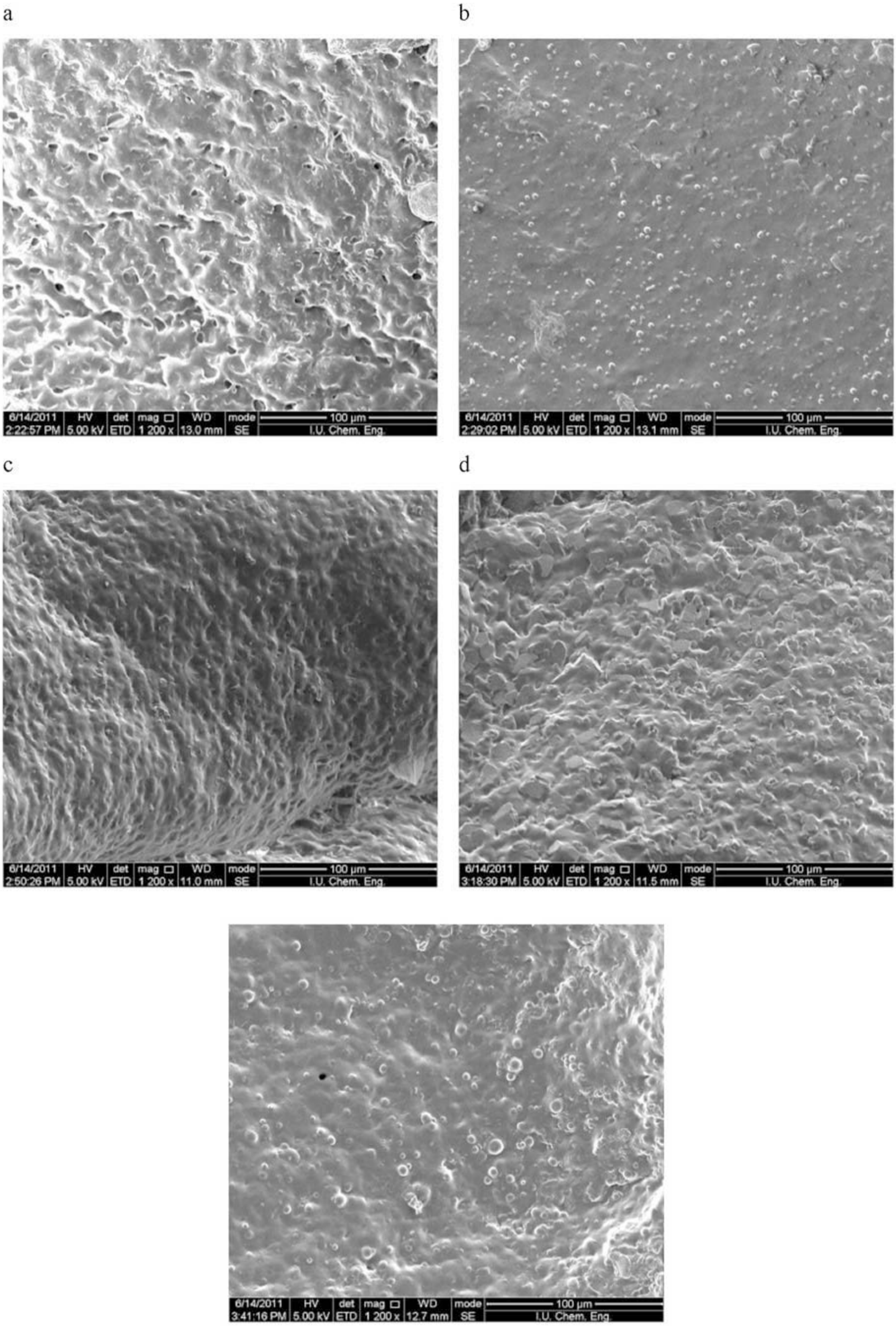

Fig. 7. SEM micrographs of the P(VC-co-DDMA) gel in: heptane (a), toluene (b), and {heptane + toluene} mixtures with toluene content/mass %: 20 (c), 50 (d), and 70 (e).

Table 3. Parameters of the power-law model

	Power-law model				
	k	n	Diffusion mechanism	R^2	RMSD
in heptane	0.51	0.41	Fickian	0.977	0.15
in toluene	0.20	0.59	non-Fickian	0.988	1.17
20 mass % of toluene					
heptane	0.25	0.49	Fickian	0.967	0.14
toluene	0.26	0.47	Fickian	0.971	0.30
30 mass % of toluene					
heptane	0.19	0.60	non-Fickian	0.964	0.42
toluene	0.16	0.70	non-Fickian	0.982	0.21
50 mass % of toluene					
heptane	0.12	0.63	non-Fickian	0.985	0.46
toluene	0.11	0.65	non-Fickian	0.993	0.47
70 mass % of toluene					
heptane	0.16	0.52	non-Fickian	0.909	0.23
toluene	0.13	0.68	non-Fickian	0.996	0.67

of the gels. The difference in the morphology of the gels swelled in different solvents and solvent mixtures can be clearly seen. The heptane swollen gel in dry form displays more porous structure compared to its toluene swollen counterpart in dry form. Porous structure of the gel swelled in the solvent mixture with the highest heptane content (Fig. 7c) is remarkable. The SEM micrograph of the gel swelled in the solvent mixture with the highest toluene content (Fig. 7e) is similar to that of the toluene swollen gel (Fig. 7b).

Conclusions

Swelling data of the poly (*N*-vinylcaprolactam-*co*-dodecyl methacrylate) gel in heptane, toluene, and their mixtures with the toluene concentration of 20 mass %, 30 mass %, 50 mass %, and mass 70 % were obtained gravimetrically and by gas chromatography. The highest and the lowest total swelling values of the gel were obtained in toluene and heptane, respectively, considering the dynamic swelling behavior of the gels. Increasing the concentration of toluene in the {heptane + toluene} mixture also causes an increase in the total swelling value of the gel. Selectivity of the gel at different compositions of the {heptane + toluene} mixtures was also calculated and it was found to be close to 1. Experimental swelling values were correlated by first- and second-order models; the best fit of all experimental data was obtained using the second-order model. Diffusion coefficients of each component in the mixtures were also calculated using Eqs. (6) and (14). The diffusion mechanism was found to be Fickian for the gel swelled in heptane and non-Fickian for the gel swelled in toluene. The value of kinetic constant, n, indicates that also the swelling is mainly Fickian for the gel in heptane and non-Fickian for the gel in toluene. However, the diffusion mechanism is much more complicated in mixtures, i.e. while Fickian diffusion of each component absorbed by the gel in the mixture with 20 % of toluene occurs, each component in mixtures with 30 %, 50 % and 70 % of toluene causes non-Fickian character of the process. It can be concluded that the gel in each component of the mixture with higher concentration of heptane shows Fickian behavior. Despite the Fickian behavior in heptane, an increase in the toluene concentration causes non-Fickian behavior of each component in the mixtures. Interaction between toluene and heptane and higher swelling ability of the gel in toluene are probably responsible for this effect.

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