Gel Swelling Induced by Organic Vapors; Fast Transient Fluorescence Study

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Slow release from gels in various solvents: a fluorescence study

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Abstract

A novel in situ steady state fluorescence experiment was performed for studying slow release processes in gels formed by free radical cross-linking copolymerization of methyl methacrylate and ethylene glycol dimethacrylate. Gels were prepared at 75 °C with pyrene (P_y) as a fluorescence probe. After drying these gels, slow release experiments were performed in various solvent with different molar-volume, V and solubility parameters, δ at room temperature by real-time monitoring of the P_y fluorescence intensity. Slow release diffusion coefficients (D) were measured and found to be in between 0.23×10^{-6} and 2.06×10^{-6} cm^2 s^{-1} depending on the solvent used.

Keywords: Fluorescence; Gels; Solubility; Molar volume; Swelling; Slow release

1. Introduction

The slow release kinetics of physical and chemical gels are very important in many technological applications, especially in pharmaceutical and agricultural industries. The slow release process of chemically cross-linked gels can be understood by considering the osmotic pressure versus the restraining force [1–5]. The total free energy of a chemical gel consists of bulk and shear energies. In fact, in a swollen gel the bulk energy can be characterized by the osmotic bulk modulus K, which is defined in terms of the swelling pressure and the volume fraction of polymer at given temperature. On the other hand, the shear energy which keeps the gel in shape can be characterized by shear modulus G. Here shear energy minimizes the non-isotropic deformations in gel. The theory of kinetics of swelling for a spherical chemical gel was first developed by Tanaka and Filmore [6] who assumed that the shear modulus, G is negligible compared to the osmotic bulk modulus. Later, Peters and Candau [7] derived a model for the kinetics of swelling in spherical and cylindrical gels by assuming non-negligible shear modulus. Recently, Li and Tanaka [1] develop a model where the shear modulus plays the important role of keeping the gel in shape due to coupling of any change in different directions. This model predicts that the geometry of the gel is an important factor, and swelling is not a pure diffusion process.

Several experimental techniques have been employed to study the kinetics of swelling, shrinking and drying of chemical and physical gels among which are neutron scattering [8], quasi-elastic light scattering [7], macroscopic experiments [2] and in situ interferometric [9] measurements. Recently, in situ steady state fluorescence (SSF) method has been used to study sol–gel phase transitions in free radical cross-linking copolymerization (FCC) process [10–13]. Same technique was also applied for studying swelling and drying processes in various gel systems [14–16].

It has been known that SSF spectra of many chromophores are sensitive to their environment. The interaction between the chromophore and the solvent molecules affect the energy difference between the ground and the excited states. This energy difference is called stokes shift, and depends on the refractive index and

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dielectric constant of the solvent. Recently, by measuring the stokes shift of a polarity sensitive fluorescent species, the gelation during epoxy curing was monitored as a function of cure time [17]. A pyrene (P_y) derivative was used as a fluorescence molecule to monitor the polymerization, aging and drying of aluminosilicate gels [18]. Volume phase transition of poly(acrylamide) gels were monitored by fluorescence anisotropy and lifetime measurements of dansyl groups [19].

In this work, slow release processes of gels formed by solution FCC of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDM) were studied. P_y is used as a fluorescence probe to monitor slow release processes during in situ fluorescence experiments in various solvents with different molecular sizes and solubility parameters. In situ, SSF experiments were performed for real-time monitoring of slow release processes. The main goal in the present work is to study the slow release process in various solvents to determine the relation between the diffusion and solvent quality. Slow release diffusion coefficients, (D) were measured and found to be in between 0.23×10^{-6} and 2.06×10^{-6} $cm^2\,s^{-1}$.

2. Fluorescence method

Fluorescence and phosphorescence intensities of aromatic molecules are affected by both radiative and non-radiative processes [20]. If the possibility of perturbation due to oxygen is excluded, the radiative probabilities are found to be relatively independent of environment and even of the kind of molecules. Environmental effects on non-radiative transitions which are primarily intramolecular in nature are believed to arise from the breakdown of the Born–Oppenheimer approximation [21]. The role of the solvent in such a situation is to add the quasi-continuum of states to satisfy energy resonance conditions. The solvent acts as an energy sink for rapid vibrational relaxation which occurs after the rate limiting transition from the initial state. Years ago, Birks et al. studied the influence of solvent viscosity on the fluorescence characteristics of P_y solutions in various solvents and observed that the rate of monomer internal quenching is affected by solvent quality [22]. As the temperature of liquid solution is varied, the environment about the molecule changes and much of the change in absorption spectra and fluorescence yields in solution can be related to the changes in solvent viscosity. A matrix that changes little with temperature will enable one to study molecular properties themselves without changing environmental influence. Polymethyl methacrylate (PMMA) has been used as such a matrix in many studies [23]. It has been reported that viscosity of solvent affects the low frequency intramolecular vibrational energies of excited naphthalene in swollen PMMA latex particles [24].

3. Experiments

EGDM has been commonly used as cross-linker in synthesis of polimeric networks [25]. In this work the monomers MMA (Merck) and EGDM (Merck) were freed from the inhibitor by shaking with a 10% aqueous KOH solution, washing with water and drying over sodium sulfate. They were then distilled under reduced pressure over copper chloride. The polymerization solvent, toluene (Merck), was distilled twice over sodium. The radical copolymerization MMA and EGDM was performed in toluene (0.2 vol%) at 75 °C in the presence of 2,2′-azobisisobutyronitrile (AIBN) an initiator. AIBN (0.26 wt.%) was dissolved in MMA and transferred into round glass tubes of 9.5 mm internal diameter. P_y was added as a fluorescence probe before the gelation process during sample preparation. Here P_y concentration was taken as 4×10^{-4} M. All samples were deoxygenated by bubbling nitrogen for 10 min and then radical copolymerization of MMA and EGDM was performed. The monomer (MMA), cross-linker agent (EGDM) and toluene were purchased from Merk Co. After the gels are formed they are cut into disc shaped to use in swelling and slow release experiments. Four different solvents with different molar volume and solubility parameters were chosen for slow release experiments. Spectroscopically pure grade ethyl acetate (EA), chloroform (CH), dichloromethane (DM) and acetone (AC) were purchased from Merck Co. and used as they are. Characteristics of solvents are listed in Table 1.

SSF measurements were carried out using a Perkin Elmer model LS-50 spectroflurimeter. All measurements were made at the 90° position and slit widths were kept at 10 nm. In situ slow release experiments were both performed in a 1×1 cm^2 quartz cell at room temperature. Gel samples were attached to one side of the quartz cell by pressing the disc with thin steal wire. The quartz cell was filled with AC, CH, DM and EA for slow release experiments. This cell was placed in the spectrofluorimeter and fluorescence emission was monitored at a 90° angle. Two different experiments were carried out for two different position of the gel samples for each set of experiment (see Fig. 1). In both experiments identical disc shaped gels were used which were dried cut from the cylindrical gels obtained from FCC. The thickness of these disc shaped gels were around 0.13 cm. In the first position only the gel was illuminated by the excitation light where the total fluorescence emission, I_p caused by P_y molecules come from the P_y molecules immersed in the gel and desorbed from the swelling gel. In the second position gel sample was shifted slightly to upward position so that only the cell with solvent was illuminated by the excitation light. Here the fluorescence emission, I_d from P_y molecules which are desorbed from the swelling gel was monitored. Fig. 1a and b present the first and

Table 1
Slow release and swelling parameters of gels and characteristics of solvents

	$(a_\infty - a_0)$ (cm)	W_∞ (g)	δ (cal cm^{-3})$^{1/2}$	V (cm^3 M^{-1})	D (cm^2 sn^{-1}) $\times 10^{-6}$	η (cp) 25 °C	$(t_{SW} - t_{SR})$ (s)
Acetone (AC)	0.03	0.1681	10	73	1.63	0.306	2200
Chloroform (CH)	0.065	0.312	9.3	80	2.06	0.537	15300
Dichloro-methane (DM)	0.025	0.1874	9.7	64	0.23	0.413	21600
Ethyl-acetate (EA)	0.03	0.1661	9.1	98	0.64	0.423	5600

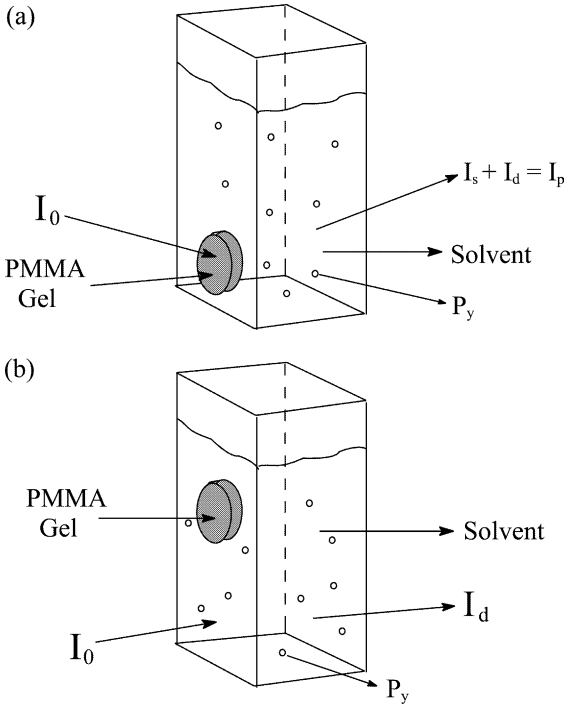

Fig. 1. Fluorescence cell in LS-50 Perkin Elmer spectrofluorimeter. Monitoring of (a) swelling and (b) slow release, processes. I_0 and $I_p = I_s + I_d$, I_d are the excitation and total emission intensities at 345 and 395 nm respectively.

second position of the gels respectively. These experiments are repeated for each solvent.

When P_y molecules are excited at 345 nm typical emission spectra of P_y is presented in Fig. 2. During the experiments the wavelength of the excitation light was kept at 345 nm and P_y intensities was monitored at 395 nm using the time drive mode of spectrofluorimeter. No shift was observed in the wavelength of maximum intensity of P_y and gel samples were kept their transparencies during the experiments. Slow release curves of P_y molecules were used to obtain pure swelling curves by subtracting the intensities taken from samples at the position given in Fig. 1a and b. In swelling experiments continuous volume transitions are expected which

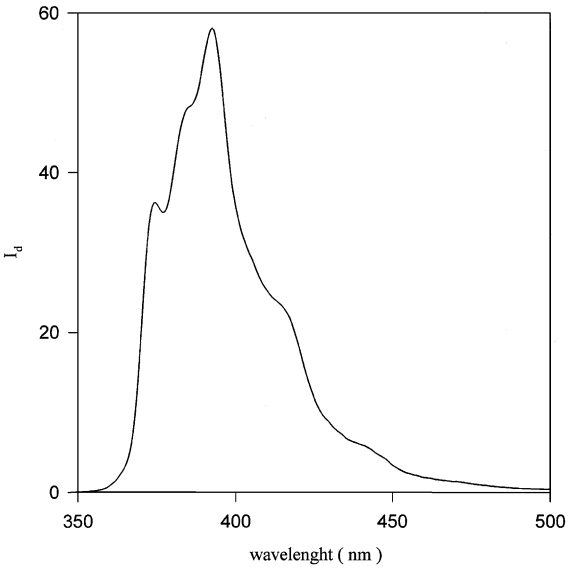

Fig. 2. Emission spectra of P_y taken after the slow release process is completed in chloroform. P_y is excited at 345 nm.

should result continuous decrease in I_p during swelling. Here one may expect that as solvent uptake (W) increases, slow release of P_y molecules from the swollen gel increases, as a result P_y intensity in the first position (I_p) decreases. On the other hand, during slow release experiments one should expect an increase in I_d, due to increasing amount of P_y molecules which are released into solvent in the cell.

4. Results and discussions

At the beginning when all P_y molecules are in the gel P_y intensity I_{os} is obtained. After solvent penetration starts, some P_y molecules are washed out and quenched from the swollen part of the gel into the cell, as a result P_y intensity, I_s from glassy part of the gel decrease as slow release time increase. At the equilibrium state of swelling, P_y intensity from glassy gel reaches to $I_{\infty s}$ value where the solvent uptake by swollen gel is W_∞. The

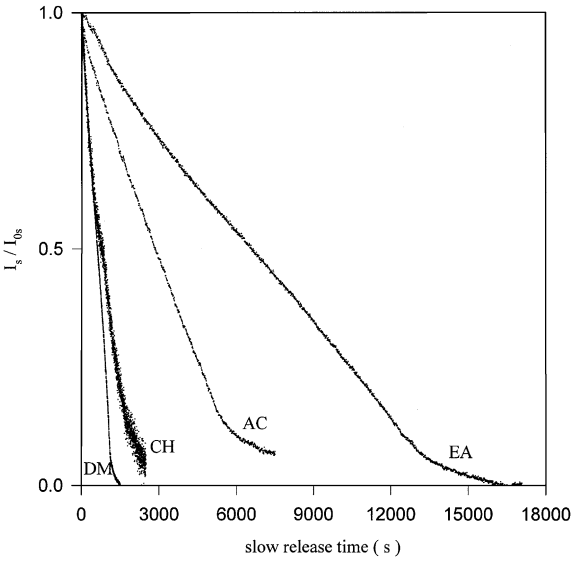

Fig. 3. Normalized P_y intensity, from the glassy part of the gel samples listed in the Table 1. The gel in the cell was illuminated at 345 nm during swelling measurements. Data for the plot were obtained using time drive mode of the spectrometer.

relation between solvent uptake W and fluorescence intensity, I_s from the glassy part of gel is given by the following relation:

$$\frac{W}{W_\infty} = \frac{I_{os} - I_s}{I_{os} - I_{\infty s}} \tag{1}$$

Since $I_{os} \gg I_{\infty s}$, then Eq. (1) becomes

$$\frac{W}{W_\infty} = 1 - \frac{I_s}{I_{os}} \tag{2}$$

this relation predicts that as W increases I_s decreases and is quite similar to the equation, used to monitor oxygen uptake by PMMA and poly vinyl acetate spheres [26,27].

If one thinks that the fluorescence intensity curves, I_p are originated only from the gels, then Eq. (2) has to be obeyed by the data. However, during the swelling experiments, desorbing P_y molecules also contribute to the fluorescence intensity, which prevents us to observe pure swelling curves. In fact I_p data present the total P_y intensity, in Fig. 1a during in situ swelling experiments, which are presented by the following relations at times

$$\begin{aligned} &t = 0, \quad I_{op} = I_{os} + I_{od} \\ &t > 0, \quad I_p = I_s + I_d \\ &t = \infty, \quad I_{\infty p} = I_{\infty s} + I_{\infty d} \end{aligned} \tag{3}$$

where I_d is the P_y intensity from the desorbing P_y molecules as shown in Fig. 1b.

In order to produce the pure swelling intensity (I_s) curves, I_d data are subtracted from the I_p data for each swelling experiment according to Eq. (3) and plotted in Fig. 3 for AC, EA, CH and DM solvent.

5. Slow release

Using the I_s curves in Fig. 3 and employing Eq. (2), the solvent uptake ratios W/W_∞ are obtained and plotted in Fig. 4a and b for AC and CH respectively. It is seen that solvent uptake increase for all solvents as I_s/I_{os} ratio is decreased. In Fig. 4a and b the results of the slow release experiments for AC and CH are also presented where I_d increases as slow release time is increased. Since I_d is directly proportional to the number of P_y molecules in solvent, the behavior of I_d curves in Fig. 4 suggest that P_y molecules are desorbed more slowly than solvent uptake by the gels. In other words, slow release of P_y molecules continue even after the equilibrium swelling of the gel has been reached. The slow release process can be treated using the Fickian diffusion model [28]. The slow release (I_d) curves in Fig. 4 support this suggestion. The

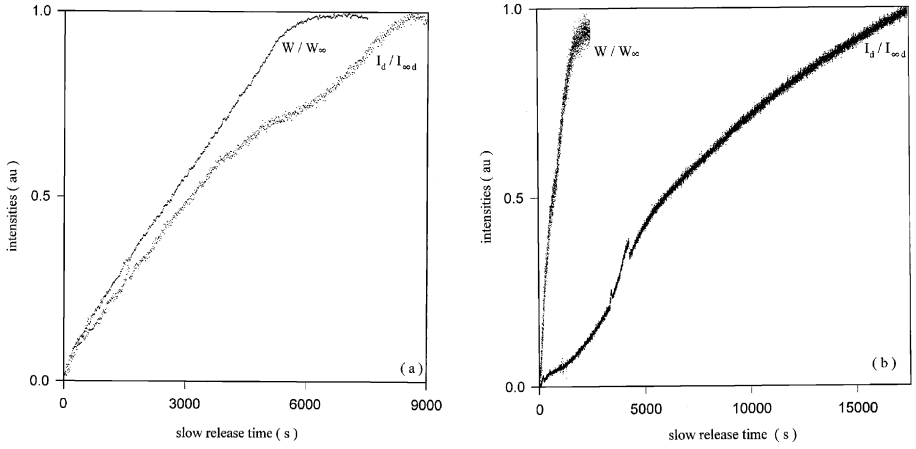

Fig. 4. Solvent uptake (W/W_∞) and slow release ($I_d/I_{\infty d}$) curves for the gel samples in (a) AC and (b) CH.

desorption transport from a thin slab is given by the following relation

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{8}{(2n+1)^2}\exp\left(-\frac{(2n+1)^2 D\pi^2}{a_0^2}t\right) \quad (4)$$

where D can be called slow release diffusion coefficient, M_t the amount of P_y molecules released at time t and M_∞ its equilibrium value at $t = \infty$. Here a_0 is taken as the initial thickness of the swollen gel. If M_t and M_∞ is considered to be proportional to I_d and $I_{\infty d}$, respectively and the thin discs used are assumed to be thin slabs, then the logarithmic form of Eq. (4) for $n = 0$ can be written as follows

$$\ln\left(1 - \frac{I_d}{I_{\infty d}}\right) = \ln\left(\frac{8}{\pi^2}\right) - \frac{D\pi^2}{a_0^2}t \quad (5)$$

Slow release diffusion coefficients, D for P_y molecules can be therefore obtained using Eq. (5). The $I_d/I_{\infty d}$ data in Fig. 4a and b are fitted to Eq. (5) in Fig. 5a and b for AC and CH samples, in where slope of the linear curves produce D values which are listed in Table 1. In Fig. 5, linear fits are quite successful which states that the slow release model which is employed is reliable for the gel systems. D values for DM and EA samples are also provided in Table 1.

Now it is important to note that penetration and desorption of solvent molecules into gel should substantially depends on the hydrocarbon employed. Now the challenge is to figure out whether kinetic effects associated with the solvent viscosity (η) or thermodynamic effect (polymer–solvent interaction) are responsible for the slow release from the gel. Here it is convenient first to test whether the solvent quality i.e. polymer–solvent interaction are responsible from the swelling processes or not. Solution theory predicts that polymer–solvent interaction parameter is related to solubility parameter (δ) and molar volume (V) via the following relation [29]

$$\chi = \frac{V}{RT}(\delta - \delta_p)^2 \quad (6)$$

where R is the gas constant, T is the temperature and δ_p is the solubility parameter of the polymer. In Fig. 6a plot of D versus V shows that there is inverse correlation between these parameter except EA, i.e. slow release is faster for the larger molecule which is not meaningful at all is plotted. In Fig. 6b, plot of D versus δ shows that correlation is still poor between these parameters to reach any serious conclusion. In Fig. 7, we try to plot D values against solvent viscosity, η. It presents quite successful correlation between these parameters except AC sample. From here one may conclude that neither the kinetic nor the thermodynamic effects are responsible from the slow release processes from gels.

In Fig. 8, slow release diffusion coefficient D versus $(a_\infty - a_0)$ is plotted where very successful correlation is observed (where a_∞ is the final thickness of the gel). This relation can be explained by the following arguments. As the network is swollen by absorption of solvent, the chains between network junction are required to assume elongated configurations, and a force akin to the swelling process. As swelling proceeds this force increases and the dilution force decreases. If one assumes that $(a_\infty - a_0)$ is the measure of the force of retraction in a stretched network structure, then, as the gel swells, higher force of retraction is applied, as a result D presents larger value, as in CH. However smaller $(a_\infty - a_0)$ causes smaller D value, as in DM. Here one can conclude that the size of a swollen gel plays an important role during slow release processes.

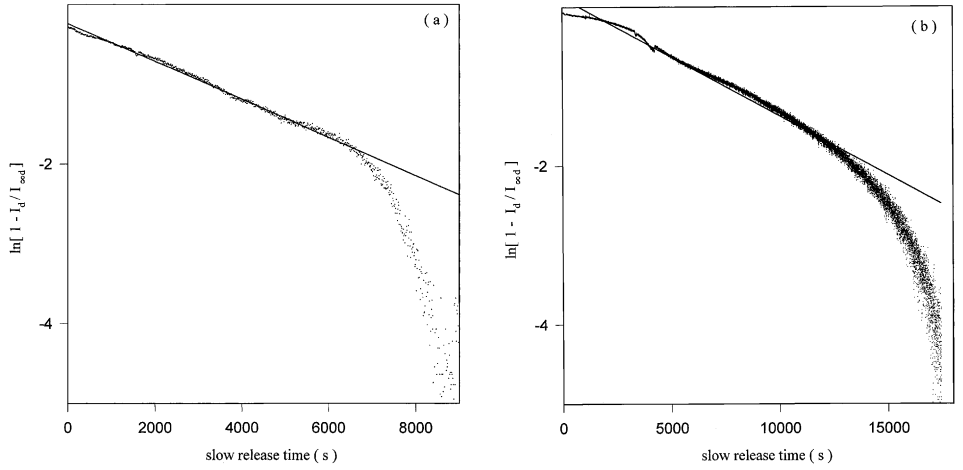

Fig. 5. Fit of the slow release data in Fig. 4 to the Eq. (5) for the gel samples in (a) AC and (b) CH. Slope of the curves produce slow release diffusion coefficients for the corresponding samples.

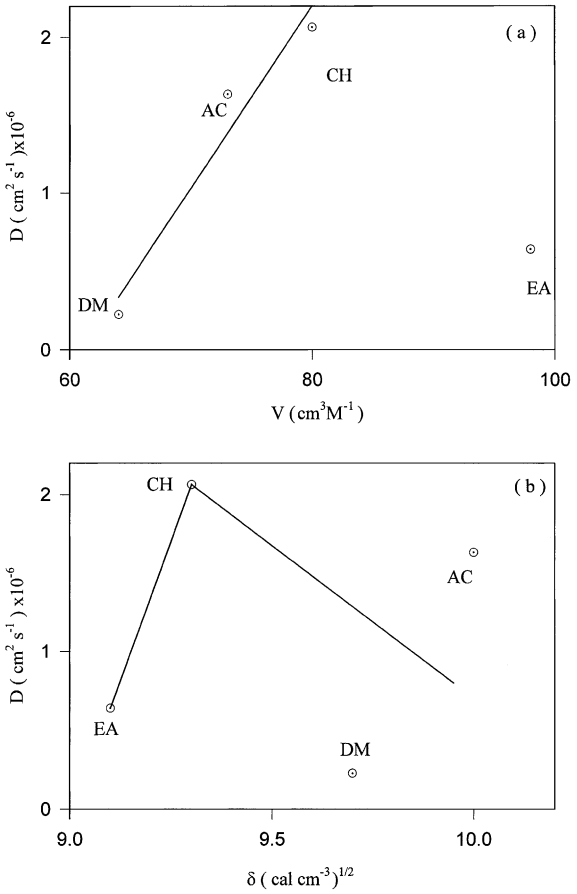

Fig. 6. Plot of slow release diffusion coefficients, D versus (a) molar volume, V and (b) solubility parameter, δ of the solvent that are used.

When one compares the swelling (W) and slow release (M_t) data in Fig. 4, all gel samples present a certain delay between the equilibrium values. Fig. 4 shows that slow release of P_y molecules continuous even after complete swelling is reached. For instance 75% of P_y molecules are released when the gel has reached complete swollen state in CH. The time delay is even more dramatic when the gel is in DM, where 15% of P_y molecules are released after the gel is completely swollen. Delay in time of swelling and slow release processes can be measured with the parameter of $(t_{SW} - t_{SR})$, where t_{SW} corresponds to the time for complete swelling and t_{SR} is the time for the end of slow release processes respectively. In Table 1, $(t_{SW} - t_{SR})$ values are given for all gel samples. In order to understand the mechanism of time delay between swelling and slow release process; solvent viscosity (η) versus $(t_{SW} - t_{SR})$ is plotted in Fig. 9a, where correlation has some success except DM sample. As viscosity of solvent is increased time delay between swelling and slow release increases in other

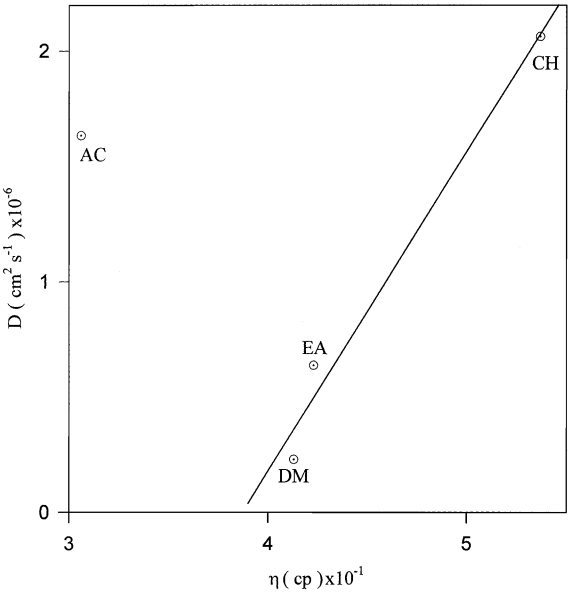

Fig. 7. Plot of slow release diffusion coefficients, D versus viscosity, η of the solvents that are used in slow release experiments.

words high viscosity causes slower release of solvent molecules from the swollen gel except DM. In Fig. 9b, $(t_{SW} - t_{SR})$ versus solubility parameter, δ is plotted, where meaningful correlation can be seen, if one realizes the fact that DM is the smallest molecule among others.

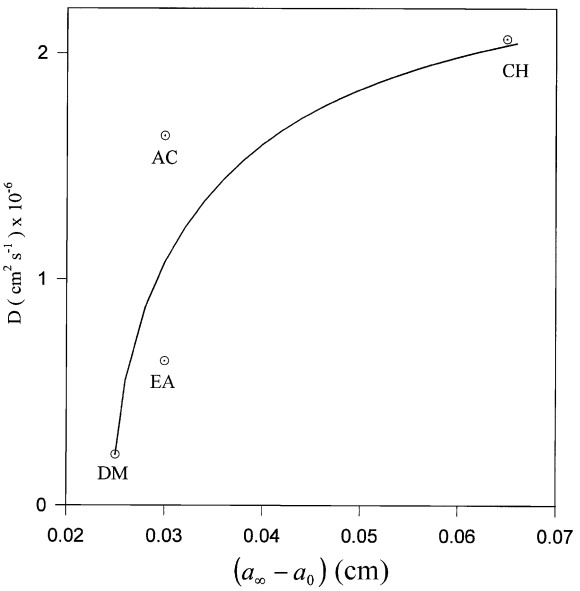

Fig. 8. Plot of slow release diffusion coefficients, D versus $(a_\infty - a_0)$ where a_0 and a_∞ are the initial and final thickness of the gel samples in solvents.

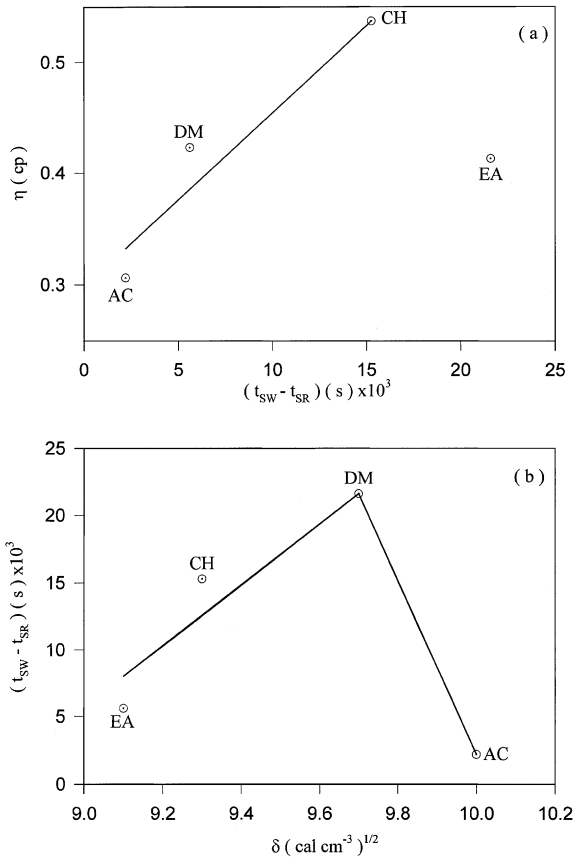

Fig. 9. Plot of time delay, ($t_{SW} - t_{SR}$) between swelling and slow release processes versus solvent (a) viscosity, η and (b) solubility parameters, δ. Here t_{SW} and t_{SR} present the times of complete swelling and slow release processes.

Here it can be stated that high polymer–solvent interaction causes a larger time delay between swelling and slow release processes i.e. if polymer of the gel likes the solvent, slow release of solvent molecules slows down and results a delay in release time. We try to plot other parameters such as V, D and ($a_\infty - a_0$) against ($t_{SW} - t_{SR}$), but no correlation is observed between them. From here, we conclude that thermodynamic effect presented by solubility parameter (δ) is responsible from the delay between swelling and slow release processes.

In conclusion these preliminary results showed that the SSF method can be used for real time monitoring of the slow release processes. However, we need more experiments with more different solvent and with different gel systems to understand the real mechanism for the time delay between swelling and slow release processes.

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