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Dynamic Behavior and Mass Transport in Polyacrylic Acid Gel by Dynamic Light Scattering

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Abstract: Dynamic behaviors on polyacrylic acid (PAA) gels and mass (small molecules) transports in the gels have been studied mainly by dynamic light scattering (DLS). The cross-linking degree (f_c), monomer concentration (C_m) and temperature of the gels have significant influences on its dynamic behavior and mass transport in the gels. The increase of f_c leads to decrease of the mesh sizes of the gels, thus the obstacle of the gels for mass transport is increased. As a result, small molecular diffusion D_k in the gels is decreased. So even if for small molecules, the D_k also is influenced.

Keywords: Polyacrylic acid gel, dynamic light scattering, mass transport, diffusion.

The mass transport in a gel is a base process in its many applications. This is why so many peoples are interested in it[1,2]. Understanding the diffusion of small molecules in gels is useful and important for the processes involving the transport in porous medium, controlled release for drugs and electrophoresis and gel filtration *etc*. But, so far, only few papers are concerned about the relationship between the dynamic behavior of the gel and mass transport of small molecules. So the simulation study on diffusion ability of small molecular probe and obstructive extent of gel is an essential and important problem.

In this paper, we present, for the first, a systematical study on the relationship between dynamic behaviors of gel and mass transport of small molecules in gel from diffusion point of view. The dynamic behavior of the gel is characterized in term of the correlation length ξ and diffusion coefficient D_t. DLS is used to determine the dynamic property of polyacrylic acid (PAA) gel. Different cross-linking degree (f_c), monomer concentration (C_m) and temperature of PAA gel were examined. $K_2Cr_2O_7$ was chosen as small molecular probe just for convenience.

Samples and measurements

The samples used in these experiments were PAA gels obtained by free-radical

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copolymerization of acrylic acid (AA) with small amounts of methylene-bis-acrylamide (MBAA) as cross-linking agent in aqueous. All reactants for DLS were filtered through 0.22 μm filters (Millipore) into dust-free ampoules directly.

The diffusion species was $K_2Cr_2O_7$ in aqueous. The gels were soaked in water solution of $K_2Cr_2O_7$ for 2 days. And then each gel was suspended in a cuvette with water, the concentration of $K_2Cr_2O_7$ in the cuvette was measured periodically to get release curve using ultra-violet spectrophotometer (WFZ800-D3A). Finally, the diffusion coefficient D_k of $K_2Cr_2O_7$ in the gel was abstracted by fitting the release curve[3].

Photon Correlation Spectroscopy (PCS) (BI-200SM spectrophotometer and BI-9000AT correlator, Brookhaven Co, USA) and argon ion laser (Innova 304, Coherent Co. USA) were used for DLS. From DLS the parameters ξ and D_t are obtained[4].

Dynamic behavior of PAA gels

We choose the varying of D_k in gel as a criterion to judge the obstacle of gel for mass transport first, and reveal what is responsible for the obstacle, then study the influence of both structure and environment on the obstacle. When the obstacle increases, the diffusion coefficient of small molecular probe in gel should be decreased.

Figure 1 shows that the mesh size ξ of PAA gels decay exponentially following the increase of the degrees of cross-linking f_c. But their diffusion coefficients D_t increased with the increase of f_c. In other words, the size of porosity of the gel will decrease following the increasing of f_c. And the influence of C_m on D_k is almost the same as the f_c. They all are reasonable.

Figure 2 is the evolution of the time correlation function. Along with the temperature raise, the correlation curve decays rapidly, *i.e.*, the cooperation diffusion coefficient D_t of the gel increase, and the mesh size ξ value lowers (**Table**) and the distribution of ξ tends to narrow.

Figure 1 The mesh size ξ of PAA gels and corresponding diffusion coefficient D_t as a function of the degrees of cross-linking f_c

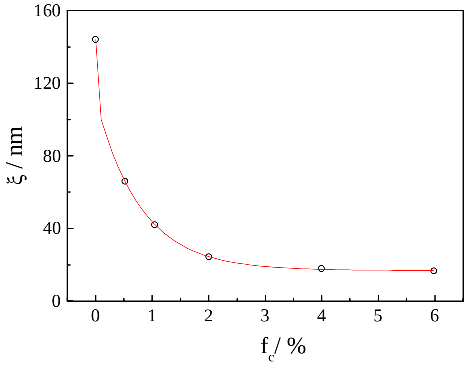


Figure 2 The evolution of correlation curve of PAA gels as a function of the temperature. $g^{(2)}(\tau)$, τ is the time correlation function of intensity-intensity, delay time, respectively

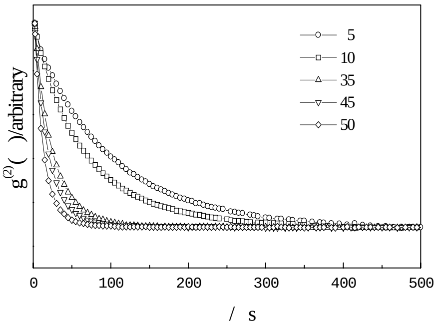


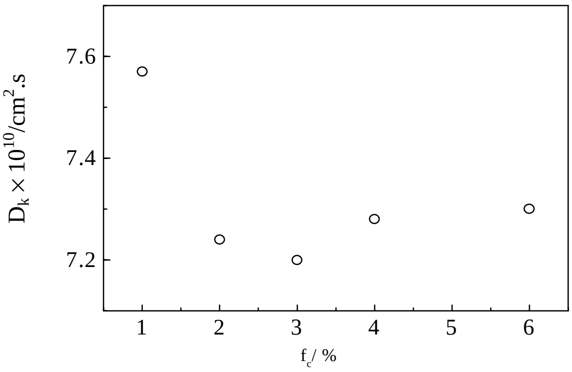
Table The ξ of PAA gels (f_c=2%) and D_k of $K_2Cr_2O_7$ in the gels at different temperature

T°C	5	10	25	35	45	50
ξ/nm	31.53	24.04	18.40	15.00	13.50	11.87
D_kx10^{10}/m^2s^{-1}	4.10	5.90	7.24	7.96	8.80	11.00

Mass transport in gel

Figure 3 is the influence of the f_c on the diffusion coefficient D_k of $K_2Cr_2O_7$ in PAA gels. Comparison with **Figure 1,** the results are as follows: when f_c vary from 1% to 6 %, the corresponding ξ decrease from 42.12 to 16.70 nm, which decrease around 86 %, but D_k are correspondingly from 7.57 to 7.25, which decrease only around 5 %. Obviously, the decrease of ξ (or porous size) implies both increasing obstacle and decreasing the diffusion coefficient D_k. Furthermore, this means although the probe molecule, $K_2Cr_2O_7$, is so small, it is big enough to be effected by the dynamic behavior of the gel. However, the influence is slight. Naturally, one will ask whether the change of 5% is error, or the influence of ξ is not existent at all. So the another evidence is necessary.

Figure 3 The influence of f_c on the diffusion coefficient D_k of $K_2Cr_2O_7$ in PAA gels



Fortunately, the dependence of D_k on temperatures can give us essential evidence. In principle, while the temperature is raised, D_k should be increased. Simultaneously, ξ will decrease (**Table**) and D_k should be decreased, if the influence of ξ on D_k really exists, *i.e.*, there are two opposite factors to exert the effects on D_k at the same time. Therefore, from the tendency of D_k and ξ in the **Table**, we still can not distinguish the influence from temperature and ξ. In other words, it is not clear that does ξ influence D_k? Is there experimental error or D_k is influenced by two opposite factors? Following analyzing may be helpful for answer this question.

To analyze the phenomenon, two kinds of ratios D_x (=D_x/D_5) for D_k have been carefully compared:

$D_5/D_{10}/D_{25}/D_{35}/D_{45}/D_{50}$ =1/1.180/1.819/2.328/2.897/3.210 (cal. by Stock-Einstein eq.)

$D_5/D_{10}/D_{25}/D_{35}/D_{45}/D_{50}$ = 1/1.439/1.766/1.942/2.146/2.707 (exp.)

The subscript x represents the experimental temperatures and we use the value of 5°C as a start point, *i.e.*, D_5. So the bigger the influence is, the higher the ratio is. Reasonably, if there is no influence of the ξ on D_k at all, the two kinds of ratios should be the same. But if the obstacle for the diffusion of small molecular probe increases due to the decrease of the ξ, the experimental ratios should be smaller than calculated one correspondingly or *vice versa*. Apparently, the latter is true. And furthermore, the higher the temperature is, the bigger the difference of the ratio is. In other words, along with raising the temperature the increase rate of D_k gets slower and slower, *i.e.*, the influence of the ξ on the D_k becomes bigger and bigger. So, it proves strongly that the obstacle of PAA gel for the diffusion of small molecular probe $K_2Cr_2O_7$ does exist. These experimental results are not only interesting but also support powerfully the previous results on the existence of the obstacle in gel even for small molecular probe. In addition, the change of ξ herein reveals that the structure of the gel is rather sensitive to the temperature (environment), and the conformation of the chains in gel is rather flexible. Essentially, the main reason for these phenomena is interaction parameter χ, which is inversely proportional to the temperature[5]. When the temperature decreases, χ becomes large, so that ξ increases. And finally, phase separation may take place for χ-induced microsyneresis[6], ξ will be large dramatically.

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References

1. J. Lee, K .Park, T. Chang, J. C. Jung, *Macromolecules*, **1992**, *25*, 6977.
2. L. Masaro, X. X. Zhu, *Macromolecules*, **1999**, *32*, 5383.
3. L. Haggerty, J.H. Sugarman, R.K .Prud'homme, *Polymer*, **1988**, *29*, 1058.
4. R. Pecora, *Dynamic Light Scattering - Applications of Photon Correlation Spectroscopy*, Ed. Plenum Press, New York and London. **1985**, P. 181, 347.
5. A. J. Chompff, *Polymer Network s- Structure and Mechanical Properties*, Plenum Press, New York and London. **1971**, P. 245.
6. J. Zuo, F. J. Zhang, Y.l. An, A. Z. Niu, Z. G. Zhang, F. X. Li, C.Y. Zhu, B. L. He, *Acta Polymerica Sinica*, **1999**, *4*, 385.

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