

NOTE

Structure of Gels Formed by Modified Poly(vinyl chloride) and Di(2-ethylhexyl)dithiophosphoric Acid

INTRODUCTION

A newly developed method of gel preparation based upon modification of poly(vinyl chloride) (PVC) by a nucleophilic agent that is compatible with the liquid PVC with which it is to be gelled was recently described.^{1,2} It was found that PVC modified by dioctyldithiocarbamate or di(2-ethylhexyl)dithiophosphate is capable of forming the gelled phases with di(2-ethylhexyl)dithiophosphoric acid (DTPA). The latter is a powerful extractant for a number of metals, which can be used in membranes^{1,3,4} or beads^{2,5} in various separation processes. Concentrated DTPA is a highly viscous liquid forming oligomers and associates.⁶

During the past few years, monitoring of polymerization reactions and the structure of polymers using fluorescent probes has been developed.^{7,8} Pyrene, a probe whose photophysics has been minutely investigated,^{8,9} was shown to form an excimer in a polymeric solution, and the ratio of pyrene monomer to excimer emission is a function of the medium viscosity.

In the present work, we studied the structure of gels formed by dialkyldithio-substituted PVC and DTPA, by monitoring the changes in the monomer/excimer emission ratio of pyrene introduced into the gels. Results obtained with different contents of the gels show that there is an agreement between the metal transfer rate through the gels depending on DTPA mobility and microviscosity compared with using pyrene. Changes in microviscosity could be explained by the rearrangement of intermolecular H-bonding in the gels.

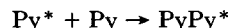
EXPERIMENTAL

Di(2-ethylhexyl)dithiophosphoric acid (DTPA) was synthesized and purified as described elsewhere.¹⁰ PVC (43 grade, Frutarom, Israel) was modified by sodium salt of DTPA as described recently.² Modified polymer (MP) containing S = 4.10%, P = 1.98%, and Cl = 42.10% was dissolved in tetrahydrofuran (THF), precipitated by methanol, and then dried. Mixtures of MP and DTPA in THF-containing pyrene were cast on Pyrex slides or NaCl

flat cells and then dried by keeping them in a closed box containing silica gel. Pyrene of A.R. grade (Fluka) was used as received. Fluorescence measurements were performed at room temperature in an SLM 8000c spectrofluorometer. Excitation wavelength and band-pass were 313 and 8 nm, respectively. Fluorescence emission experiments were run by measuring reflection at 45° from the gels cast on glass slides. IR spectra were recorded on a Nicolet 510 FTIR spectrometer in the range 4000–400 cm⁻¹ using NaCl cells.

RESULTS AND DISCUSSION

Figure 1 shows the typical emission spectra of pyrene (1.2 mM) in gels composed of different ratios of MP and DTPA. The spectra were recorded in different series of experiments. It was shown^{7,9} that the pyrene excimer formation is due to the diffusion-controlled reaction between a pyrene molecule in the excited state and another molecule in the ground state:



In our experiments, the process was characterized by a broad, structureless fluorescence emission at $\lambda = 472$ nm, which was red-shifted in respect to the fluorescence emission of the monomer ($\lambda = 396$ nm). Since the pyrene excimer formation is controlled by diffusion and is inversely proportional to the microviscosity around the probe⁷ ν , the intensity ratio R can be described by the following expression:

$$R = I_{(\text{monomer})} / I_{(\text{excimer})} = A\nu [\text{Py}]^{-1}$$

Here $[\text{Py}]$ is the concentration of pyrene and A is a constant depending mainly on instrumental characteristics.⁷

A typical result obtained in one series of experiments by monitoring the intensity ratio at 396 and 472 nm at different molar ratios (ω) of modified polymer and DTPA in the gels is presented in Figure 2 (curve 1). It can be seen that R and, thus, ν were approximately constant at $\omega = 0-0.2$, markedly decreased and reached a minimum at $\omega = 0.4-0.5$, and then smoothly increased. This result is in agreement with the data obtained recently¹ on the gels used as membranes. Curves 2 and 3 represent the silver and iron (III) transfer rates vs. ω . The mobility that

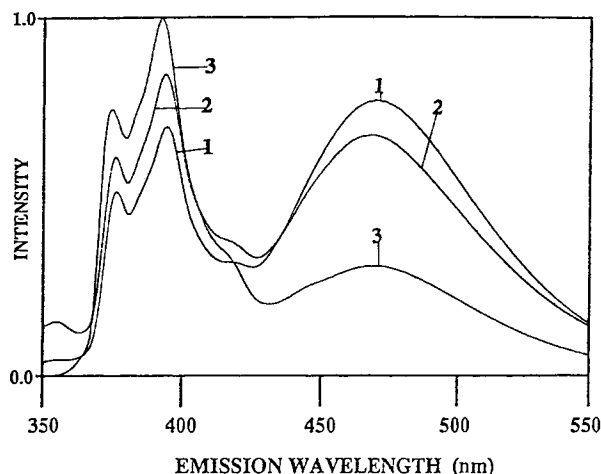


Figure 1 Typical fluorescence emission spectra of pyrene (1.2 mM) in gels formed by MP and DTPA. ω is equal to (1) 0.35, (2) 1.29, and (3) 0.12.

DTPA displayed as a metal ion carrier may depend highly on the gel microviscosity.¹¹ From Figure 2, we conclude that maximum transfer rates at $\omega = 0.4$ resulted from the minimum microviscosity at these concentrations. The slight increase of the microscopic viscosity at $\omega > 0.5$, which determined the diffusion rate through the gel, had not produced a decrease of diffusion coefficients.¹ This is additional evidence for an open structure of the gel network. The lowering of the transfer rates at above $\omega = 0.4$

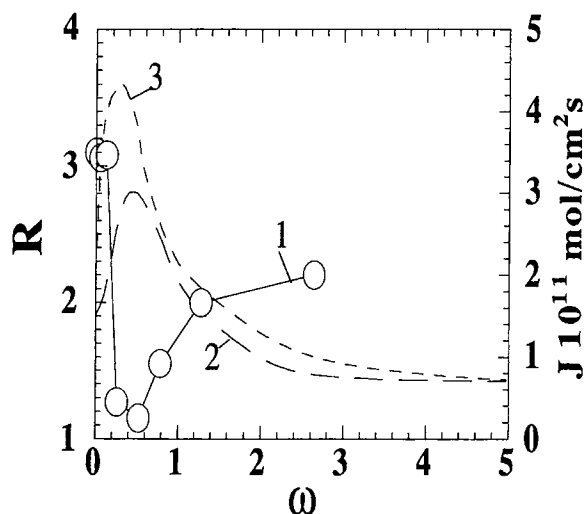


Figure 2 Dependence of the fluorescence ratio R on the polymer concentration in gel (1). $[Py] = 1.2 \text{ mM}$. R is the ratio of fluorescence intensity at 396 nm to that at 472 nm. Curves (2) and (3) developed from the data presented recently¹ show the dependencies of silver and iron (III) transfer rates (J), respectively, on the polymer/DTPA molar ratio (ω) in gel.

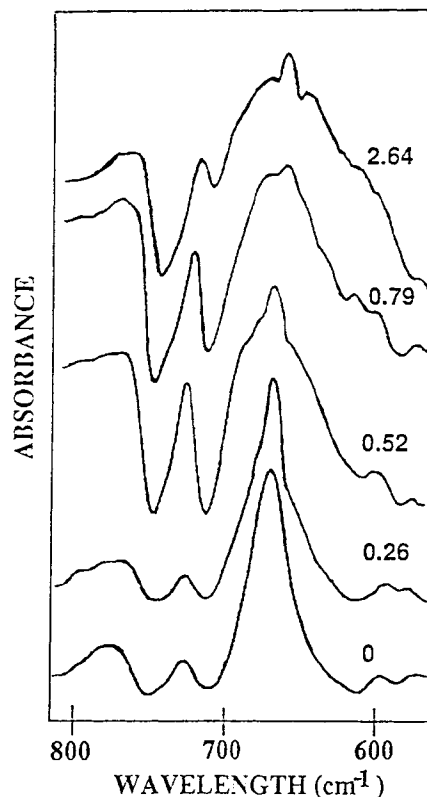


Figure 3 FTIR spectra of the gels composed of MP and DTPA. The values of ω in each sample are indicated.

in the gelled membranes may be attributed to the increase in the tortuosity of the gelled phase.

The above changes of the gel microviscosity are probably related to rearrangements of hydrogen bonds in gels. Figure 3 represents the infrared spectra of pure DTPA and different compositions of the gels. One can see that the band at 670 cm^{-1} , corresponding to the $P=S$ antisymmetric stretching¹² in pure DTPA liquid, splits in the gels. The splitting is more pronounced at higher concentration of MP. The phenomenon of the dithiophosphoryl group interaction with the electron donor groups like $P=S$, $C=S$, or $CH-Cl$ is well documented.¹³ Rearrangements of the hydrogen bonds between chlorine or sulfur atoms of MP and protons of DTPA lead to the change of $P=S$ stretching vibrations and to the observed splitting in the IR spectra. A similar effect was shown to occur when DTPA was dissolved in chlorinated hydrocarbons.

CONCLUSIONS

We have discovered by the fluorescence probe method that the newly developed gels formed by MP and DTPA possess a minimal microviscosity at $\omega = 0.4-0.5$. The metal transfer rates through the gelled membranes described recently¹ are closely related to the structure of the gels. The changes

of microviscosity may be explained by rearrangements of hydrogen bonds between MP and DTPA molecules.

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