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Physical Properties

Anomalous penetrant transport in glassy polymers

III. Use of Raman spectroscopy to study penetrant transport

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Summary

Methylene chloride transport in copolymers of poly(2-hydroxyethyl methacrylate-co-N-vinyl-2-pyrrolidone) was studied at 25 °C using Raman microprobe spectroscopy. It is shown that the abrupt change of the penetrant concentration at the rubbery/glassy interface during swelling can be detected and followed to obtain useful information about the penetrant transport mechanisms in these copolymers.

Introduction

In the two previous contributions in this series we have examined the mechanisms of penetrant transport in glassy polymers (1,2). As it is well known, penetrant transport in glassy polymers may be Fickian or non-Fickian depending on the penetrant activity, sample size and temperature of experimentation. The limiting mechanisms of this behavior are Fickian diffusion, where the penetrant uptake is proportional to $t^{1/2}$, and Case-II transport, where the penetrant uptake is proportional to the transport time, t (3).

Recently, we have also developed mathematical models (1,4) which attempt to characterize the anomalous transport in glassy polymers. Verification of these models has been achieved with gravimetric studies or spin echo NMR experiments (5). More direct model verification may be possible by analyzing the penetrant concentration profile in a polymer slab as a function of transport time. Here we present feasibility studies using Raman microprobe spectroscopy.

Raman spectroscopy is a form of inelastic light scattering which makes use of vibrational and rotational transitions in molecules to identify and quantify the absorbing or emitting functionalities. In the classical Raman experiment a monochromatic beam of light, typically generated by a laser, impinges on a sample. The emitted light consists of a very intense band of Rayleigh light and light which is not of the same frequency as the incident light and is, therefore, the result of some absorbance or radiative emission of the sample. This inelastically-scattered light may consist of many frequencies. The difference between the frequency of the incident and scattered light represents the energy of the vibrational or rotational mode which has been excited or which has decayed.

A special form of this technique is Raman microprobe spectroscopy which uses a Molecular Optics Laser Examiner (MOLE) coupled with a microscope. Using this apparatus it is possible to examine a sample as small as 1 μm^2 by using a microscope to focus and detect the laser radiation. Thus, this technique is very useful in map-

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ping the composition of heterogeneous materials. The frequency of a band of emitted light is indicative of the chemical composition of a particular chemical species. By identifying a particular frequency as belonging to a certain chemical species, the species concentration in the sample can be measured by measuring the intensity of light at its characteristic frequency.

Preparation of Polymer Samples

Copolymers of 2-hydroxyethyl methacrylate (HEMA) and N-vinyl-2-pyrrolidinone (NVP) were prepared by bulk copolymerization in the molar ratios 3:2, 2:3, and 0:1 of NVP:HEMA, respectively. The polymerization was initiated with 0.05 wt % benzoyl peroxide. Crosslinking was accomplished by incorporation of 0.15 wt % ethylene glycol dimethacrylate (EGDMA). The polymerization was conducted in Teflon® cylinders of 0.625 cm inner diameter and 10 cm long for 72 hours. The temperature was gradually increased from 40 ° to 80 ° C during the reaction. The glassy polymer cylinders were removed from their containers and stored in a dessicator.

Raman Spectroscopic Studies

Cylinders of copolymers with 2:3 NVP:HEMA were immersed in methylene chloride at 25 ° C. At regular intervals the samples were removed from the penetrant bath and cut into 1 cm thick disks. These disks were placed under the objective of the Raman MOLE instrument and a 100 mw argon laser beam at 514 nm was applied using the 100X objective of the microscope. Various points on the cylindrical crossection were examined for methylene chloride peaks in the 709 cm^{-1} shift region. The amplitude of these peaks was recorded and used to determine the relative concentrations at various points in the samples.

In addition, prior to examining the sample in the presence of penetrant, samples of the copolymer were examined in a dry state from 200 to 2200 cm^{-1} shift from the Rayleigh line. These experiments were conducted in order to determine the response of the copolymers to the Raman technique. Many polymer samples exhibit fluorescence due to extraneous electronic transitions which tend to wash out the whole spectrum. It was therefore necessary to determine the fluorescent activity.

Results of Raman Spectroscopy

Preliminary examination of dry P(HEMA-co-NVP) copolymers revealed a Raman spectrum essentially free from fluorescent interference. It is possible to identify major functional group contributions from tabulated values (6-9). The spectra of pure PHEMA and P(HEMA-co-NVP) are presented in Figures 1 and 2 along with identification of major functional groups.

Furthermore, it was possible to identify relative concentration profiles of methylene chloride in the P(HEMA-co-NVP) copolymers during swelling. Peak amplitudes for the C-Cl stretch at 709 cm^{-1} were recorded for approximately five points in each sample. This particular stretch was chosen because of the strength of absorbance and freedom of interference from other Raman peaks characteristic of the copolymer.

Figure 3 shows the methylene chloride concentration profile after 10.75 hours of diffusion. We can detect a high penetrant concentration in the rubbery portion of the polymer and a rather sharp drop in concentration near the glassy rubbery interface. These results are consistent with the dye studies of Thomas and Windle (10). Furthermore, microprobe examination of the glassy rubbery interface region revealed a sharp drop over a region of approximately 20 μm.

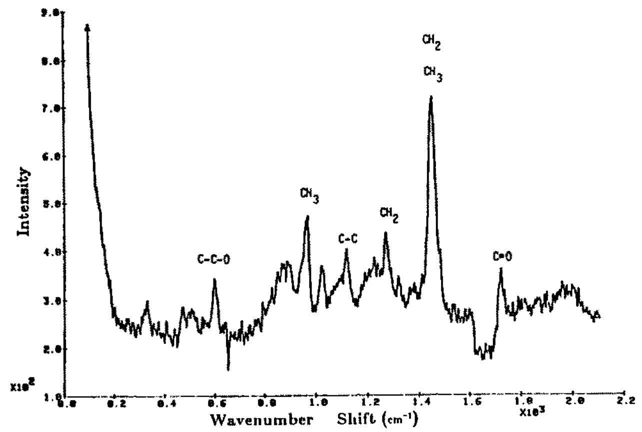

Figure 1: Raman spectrum of PHEMA showing major functionalities.

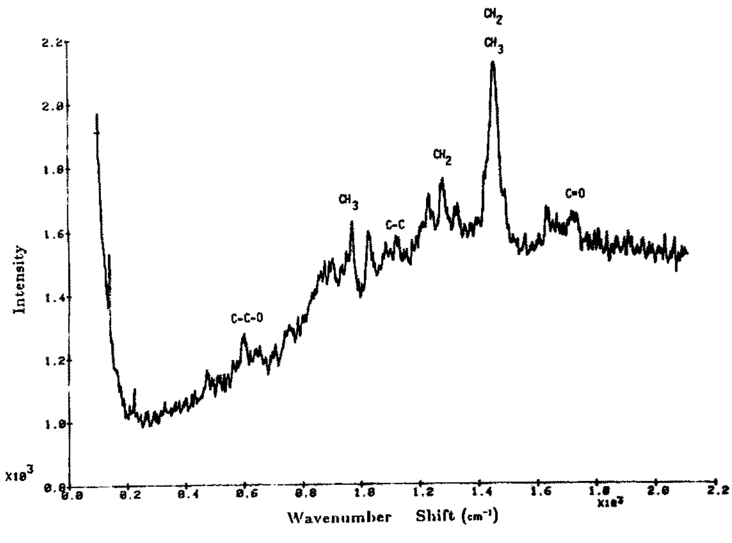

Figure 2: Raman spectrum of P(HEMA-co-NVP) showing major functionalities.

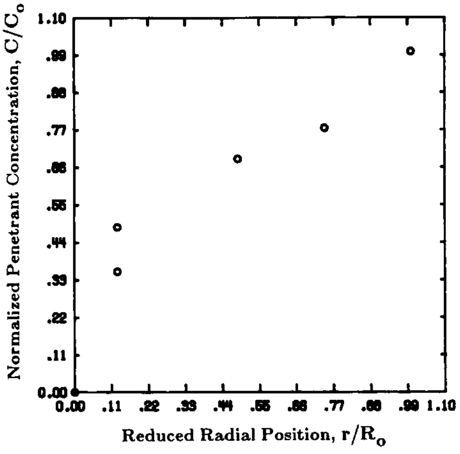

Figure 3: Methylene chloride concentration profile in cylinders of P(HEMA-co-NVP) after 10.75 hrs of swelling.

Conclusions

Raman spectroscopy is a useful technique for characterization of functional groups, examination of order disorder phenomena and quantitative characterization of polymer compounds or mixtures of polymers and "foreign" substances. Its applicability to the system of P(HEMA-co-NVP)/methylene chloride has been demonstrated. However, the instrument is less effective for examination of water penetration since the intensity of the characteristic H-O stretch at 3650 cm^{-1} is weak under Raman conditions. For greater accuracy, an internal standard is needed to calibrate the spatially scattered light.

Acknowledgments

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