Preparation of Clean Polymers for Rayleigh–Brillouin Light Scattering Studies

INTRODUCTION

In the study of glassy polymers and liquid monomers using Rayleigh–Brillouin light scattering techniques, it is important to work with clean samples. A clean sample is one which is free of chemical and physical impurities. Chemical impurities may alter the properties of the polymer. Physical impurities, such as dust, will produce large intensities of scattered light at the incident frequency. Thus, Rayleigh scattering due to the basic nature of the polymer will be masked.

The three major impurities which must be removed from a sample are inhibitor, water, and dust. Commercially available monomers normally contain an inhibitor such a hydroquinone. Styrene and the methacrylate monomers with which we have worked readily absorb water. Hence, if the inhibitor is removed by washing with a caustic solution or if the monomer is exposed to air for a length of time, the monomer will contain water. Particles of dust and other materials ranging in size from a few hundred angstroms to those visible with the naked eye constitute the physical impurities. The monomer will pick up dust from the air and from the inside of the containers in which it is placed.

In this paper we describe a technique for preparing scrupulously clean polymers in glass under vacuum.

EXPERIMENTAL

Apparatus

Because of the hygroscopic nature of these monomers it is convenient to conduct the entire preparation of samples under vacuum.

The vacuum apparatus comprises three parts: the vacuum system, the in-line filter apparatus shown in Figure 1, and the manifold shown in Figure 2. The vacuum system consists of a rotary pump, a mercury diffusion pump, a Pirani gauge to monitor the vacuum, and a cold trap. Except in the vacuum system no grease is used in the apparatus for valves or joints in order to avoid contamination of the monomer.

Technique

The manifold is first precleaned with chromic acid and rinsed with distilled water. The entire apparatus is then assembled and evacuated. To evacuate the manifold it is necessary to open valve C (Fig. 1) to bypass the millipore filter. The manifold is gently flamed with a torch while being pumped down.

After the manifold has been thoroughly flamed, all three valves are closed. The flask in which the monomer is dried (see Fig. 1) is removed and filled with monomer. A small quantity of calcium hydride briquettes are slowly added to dry the monomer. When the reaction of the calcium hydride with water in the monomer has slowed down sufficiently, a clean Teflon-coated magnetic spin bar is placed in the flask and the flask is put back on the vacuum apparatus. The monomer is frozen and the volume above it is evacuated. It is then thawed and stirred constantly for about 24 hr to dry. At this point the monomer will contain dissolved gases: oxygen and nitrogen from the air as well as hydrogen from the reaction of the calcium hydride with water. To remove these, the monomer is repeatedly frozen, pumped on, and then thawed until no more gas is liberated upon thawing.

After the final degassing, valve B is opened and about one half of the monomer is gradually distilled into the volume above the in-line filter. Ice water is normally used in the reservoir to condense the monomer. The in-line filter consists of a stainless-steel holder in which is placed a stainless-steel screen, a millipore filter, and a Teflon O-ring. These are held in place by a threaded stainless-steel ring which clamps them inside the holder. The holder has been machined to fit snugly inside a 34/45 ground-glass joint. The millipore filter is constructed of Teflon and has a pore size of 0.2 μm. It is hydrophobic, forming a barrier against free (not dissolved) water.
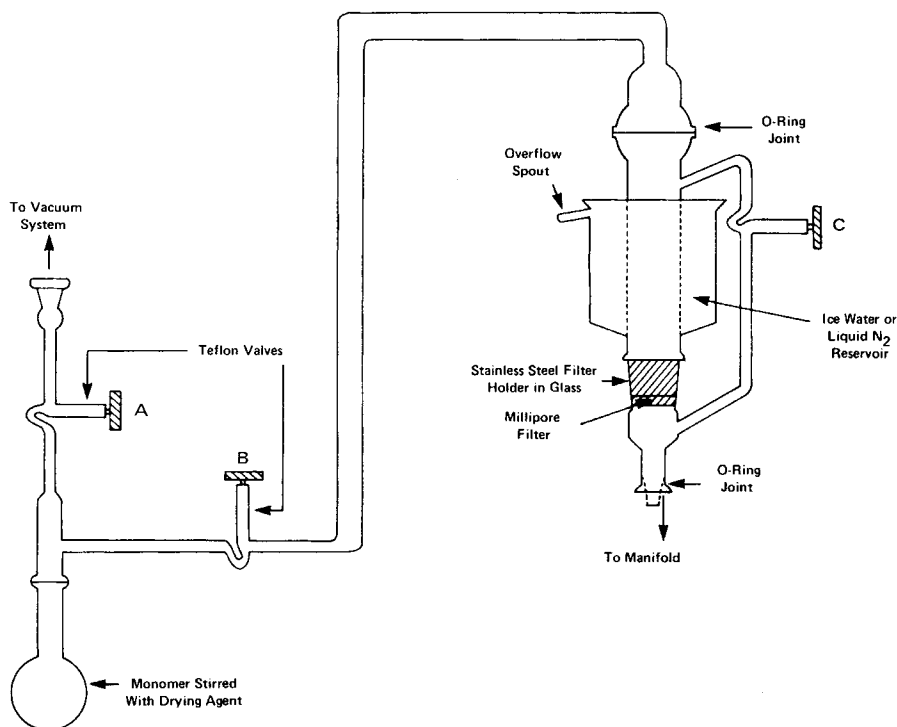
Fig. 1. In-line filter apparatus in which monomer is dried, degassed, distilled, and filtered.

When a sufficient quantity of monomer has been distilled over, the flask on the manifold is submerged in liquid nitrogen to draw the monomer through the filter. As a precaution the monomer in the manifold is further degassed. While the monomer is frozen and pumped on, the manifold is sealed off with a torch at the constriction above the flask.

At this point the manifold, sealed under vacuum, contains dry, inhibitor-free, relatively dust-free monomer. The monomer will have picked up dust from the inside of the manifold flask and will pick up more dust from the sample cells. The sample cells are now worked on one at a time, starting at the one closest to the manifold flask. Monomer is distilled into the sample cell until the cell is about half full. It is then shaken vigorously and tipped back into the flask. In this way the dust on the walls of the sample cell is washed out and into the flask. This is repeated from two to four times.
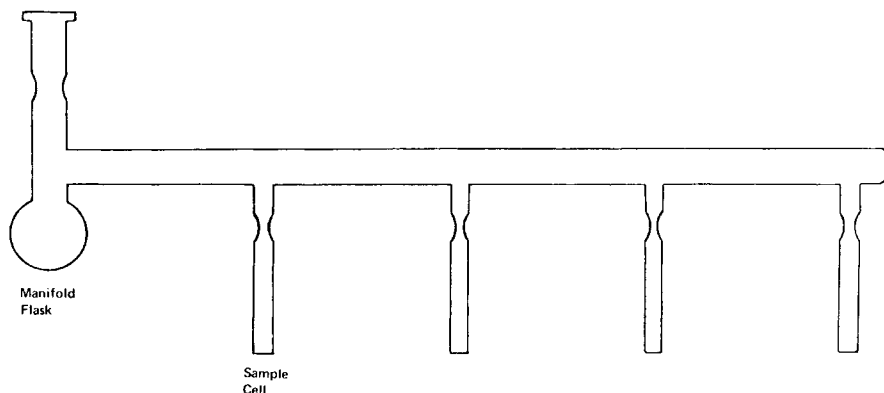

Fig. 2. Manifold. Dust-free samples are obtained by distilling monomer into a sample cell and then tipping the monomer back into the manifold flask to remove dust from the sample cell.
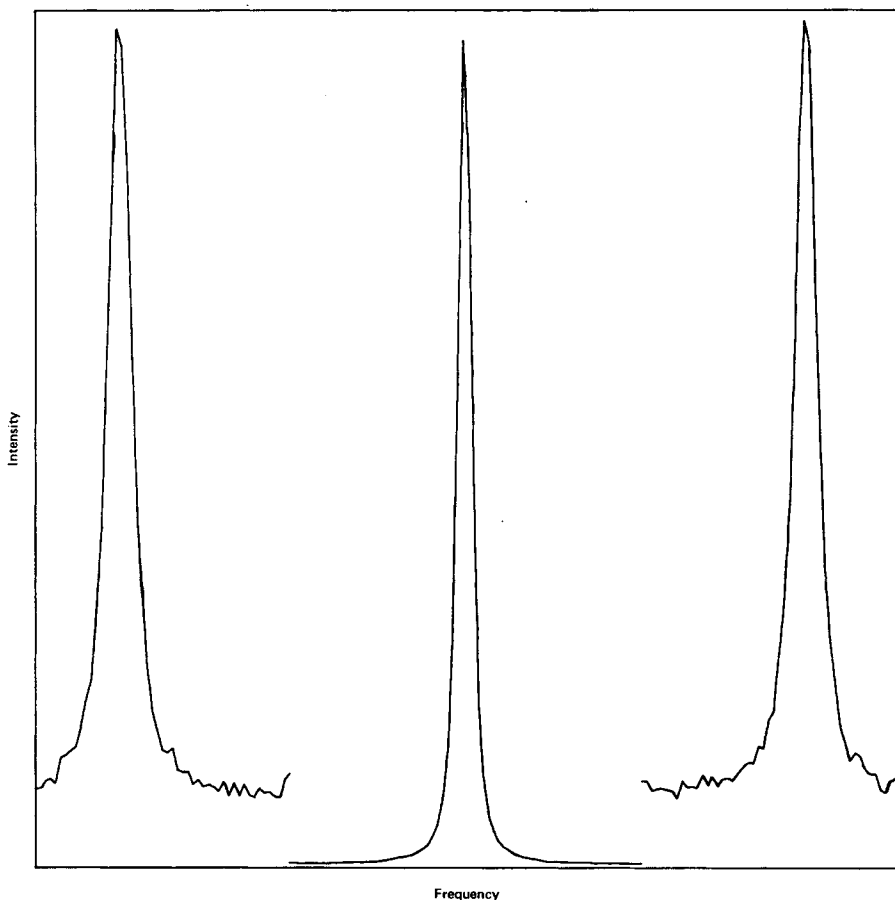
Fig. 3. Typical Rayleigh–Brillouin spectrum for polystyrene at room temperature. The vertical scale factor for the Brillouin doublet is 20 relative to the central peak.

Monomer is then slowly distilled into the sample cell until the cell is about three fourths full. The monomer in the flask and in the cell is frozen simultaneously and the cell is sealed off with the torch. This is repeated for the remaining cells. The samples are then thermally polymerized.

RESULTS

The absence of significant amounts of water in the sample is easily verified by simple observation. When the monomer is frozen, any water present will freeze first and snow upward to the surface of the monomer. Upon thawing the monomer the thin layer of snow will be the last to melt. When it does melt, it will form a small sphere of water which will sink to the bottom of the monomer. We have looked for the presence of water in prepared methylmethacrylate monomer using infrared spectroscopy. No water was found in the monomer.

Because the inhibitors that are used are usually large organic molecules, they are not expected to distill readily. Thin-layer chromatography was employed to look for residual inhibitor in a prepared styrene sample. The chromatograph for neat styrene monomer was compared with prepared styrene monomer. No inhibitor was observed in the prepared monomer.

The Rayleigh–Brillouin light-scattering spectrometer provides a very good indication of the relative amount of physical impurities in a sample (see Fig. 3). In Rayleigh–Brillouin light scattering the incident light of frequency ω_0 is scattered at this frequency by nonpropagating density fluctuations, some of which are centered on inhomogeneities such as dust particles or voids. The incident light is also scattered by thermally driven propagating density fluctuations at frequencies $\omega_0 \pm \omega$ (Bril-

louin).   Therefore, the ratio of the intensity of light scattered at the incident frequency (central component or Rayleigh) to the Brillouin doublet intensity provides a good measure of the physical purity of the sample under investigation.

Coakley, Mitchell, Stevens, and Hunt[1] have combined theory with experiment to show that the intensity ratio for clean polystyrene at room temperature should be about 5.   With the technique outlined in this paper, we have produced glassy polystyrene samples with an intensity ratio at room temperature of about 5.6 and poly(ethyl methacrylate) with an intensity ratio at room temperature less than 5.

CONCLUSIONS

We believe that the technique described in this paper produces glassy polymeric samples with the quality required to carry out meaningful studies of the intensity of light scattered by such samples.

References

1. R. W. Coakley, R. S. Mitchell, J. R. Stevens, and J. L. Hunt, *J. Appl. Phys.*, **47**, 4271 (1976).

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