Temperature, a Simple and Efficient Tool for the Control of Pore Size Distribution in Macroporous Polymers

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Introduction. Macroporous polymers are characterized by their rigid porous matrix that persists in both the swollen and dry states. The techniques for their preparation were developed in the second half of the 1950s.[1] These polymers have been produced almost exclusively as spherical beads by a suspension polymerization process and used for the preparation of ion-exchange resins, chromatographic separation media, catalysts, adsorbents, etc. The macroporous structure results from the phase separation that occurs during polymerization when the polymerization mixture contains both cross-linking and porogenic agents.[2−4] Unfortunately, there are no exact rules for the selection of polymerization conditions, and optimization experiments must be carried out for each monomer system selected. Typically, porous properties are controlled by the type of porogen selected and the amounts of both porogen and cross-linker used (e.g., refs 5−9). These variables are closely related to the solubility of the polymer molecules in the polymerization system. In contrast, much less is known about the effects of other variables such as concentration and type of free-radical initiator or polymerization temperature, which both affect the kinetics of the polymerization. Horak carried out suspension polymerizations at two different temperatures and observed a small difference in the pore sizes of poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) beads that were obtained.[6] An effect of temperature on the porous properties has also been observed during the preparation of poly(styrene-*co*-divinylbenzene)[10] and poly(trimethylolpropane trimethacrylate).[11] However, these are isolated observations and no systematic work has been published on this topic despite the obvious connection between phase separation, solubility, and temperature.

Recently, we have studied the formation of porous structure during bulk polymerization in a closed mold.[12] As we slowed the kinetics of the free-radical polymerization by lowering the reaction temperature, we found that the desired decrease in reaction rate was accompanied by a significant change in the pore size distribution of the resulting product. This report outlines the critical effect of temperature on the porous properties of beads and monoliths prepared by both suspension and bulk polymerization. Our findings provide a new approach to the control of porous properties in macroporous polymeric media.

Experimental Section. *Polymerization Mixtures.* Two different polymerization mixtures were used for the preparation of porous materials. The first was a mixture consisting of 24% glycidyl methacrylate, 16% ethylene dimethacrylate, 54% cyclohexanol, and 6% dodecanol in which azobis(isobutyronitrile) (1% of the weight of monomers) was dissolved. The second contained 30% glycidyl methacrylate, 20% diethylene glycol dimethacrylate, and 50% toluene in which azobis(isobutyronitrile) or benzoyl peroxide (1% of the weight of monomers) was dissolved. The mixtures were purged with nitrogen for 15 min before the polymerization. The stock polymerization mixtures were stored in a closed flask in a refrigerator at a temperature of 5 °C and consumed within 7 days.

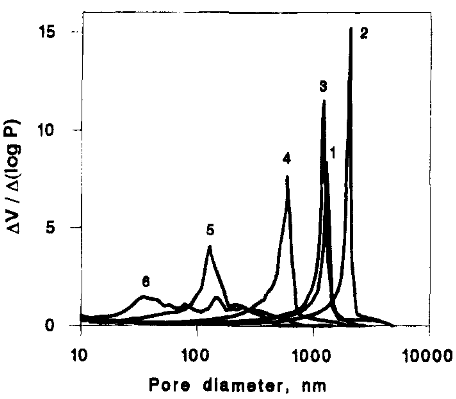

Figure 1. Differential pore size distribution curves of the poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) sheets prepared by a polymerization at a temperature of 55 (1), 60 (2), 65 (3), 70 (4), 80 (5), and 90 °C (6). For general conditions, see experimental section.

Suspension Polymerization. The polymerization mixture (4 parts) was added to a 1% aqueous solution of poly(vinylpyrrolidone) (Aldrich) MW 360 000 (6 parts) and deaerated. The polymerization was carried out in a 250 mL glass reactor (Büchi BEP 280) equipped with an anchor stirrer and a heating jacket. The beads were washed with water, extracted in a Soxhlet apparatus with methanol for 24 h, and dried at 60 °C.

Polymerization in Bulk Solution within a Mold. A flat 15 × 30 cm "sandwich" mold consisting of two Teflon plates separated with a 1.5 mm thick gasket located between two aluminum plates held together with C-clamps was charged with the polymerization mixture. The polymerization was allowed to proceed at the chosen temperature in a laboratory oven for 24 h. After the polymerization time elapsed, the mold was opened and the polymer recovered. The porous sheets were cut into small pieces with a razor blade, the soluble compounds were removed from the pores by extraction with methanol in a Soxhlet apparatus for 24 h, and the material was dried at 60 °C.

Porous Properties. The porous properties were determined by mercury intrusion porosimetry and the specific surface areas calculated from nitrogen adsorption/desorption isotherms using a custom-made combined BET sorptometer and mercury porosimeter (Porous Materials, Inc., Ithaca, NY).

Results and Discussion. Different applications of macroporous polymers require tailored pore size distributions. Currently, materials that have the same chemistry but different pore size distributions can only be prepared by polymerizing mixtures which contain different porogenic solvents. This is not very practical because a new polymerization mixture must be designed for each new porous material. Because pore formation is directly related to phase separation phenomena and these, in turn, are greatly affected by temperature, we have thought of using changes in temperature to effect changes in the porous characteristics of a specific mixture of monomers.

Bulk Polymerization. Figure 1 shows a series of pore size distribution profiles obtained for macroporous poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) sheets prepared at temperatures ranging from 55 to 90 °C.

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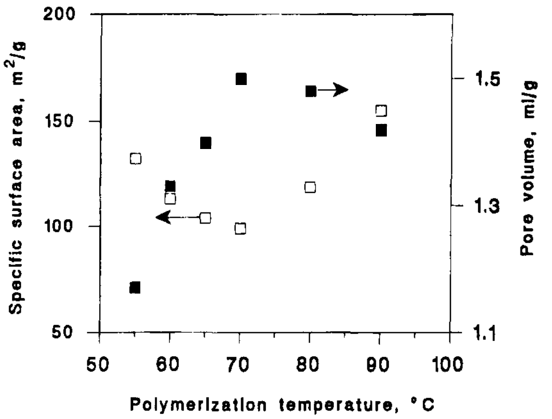

Figure 2. Effect of polymerization temperature on the specific surface area determined by BET method (□) and pore volume determined by mercury intrusion porosimetry (■) for poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) sheets.

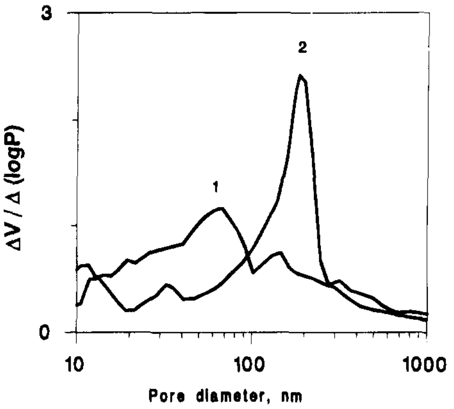

Figure 3. Differential pore size distribution curves of the poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) beads prepared by a suspension polymerization at a temperature of 90 (1) and 70 °C (2).

With the exception of the sheet obtained at 55 °C, a simple rule applies: the higher the temperature, the smaller the pores. This is not unexpected in view of the generally accepted mechanism of nucleation during polymerization in the presence of a precipitant. The polymerization mixture contains both monovinyl and divinyl monomers, initiator, and porogenic solvent. The free-radical initiator decomposes at a particular temperature and the initiating radicals start the polymerization process in solution. The polymers that are formed by solution polymerization precipitate after they become insoluble in the reaction medium as a result of both their cross-linking and the choice of porogen (poor solvent for the polymer), thus forming the nuclei. These nuclei grow to the size of globules during the continuing polymerization. The globules and their clusters constitute the elemental morphological units in the macroporous polymer. Obviously, the higher the reaction temperature, the larger the number of free-radicals that are produced and the larger the number of nuclei and globules formed. Because the amount of monomers in the system is the same for each polymerization, a higher number of globules translates into a smaller size. Because macroporous materials are composed of an array of interconnected globules, smaller voids or pores are expected if the globules are smaller.

This general rule does not apply to the polymerization at 55 °C because the initiation rate is so slow (AIBN has a half-life time of 37 h at this temperature) that other effects such as gravity[12] influence the pore formation to a greater extent.

In general, phase separation of polymers from solution is a function of temperature. With the exception of polymers with a lower critical solution temperature, the polymer–solvent mixing is an endothermic process and therefore an increase in temperature promotes dissolution of the polymers. Therefore, phase separation, which is required for the formation of macroporous structure, is likely to occur at a higher molecular weight of the nuclei during a polymerization run at a higher temperature. As a result, both the nuclei and the voids between them would be larger. Since this is actually not the case and indeed the opposite effect of temperature on pore size is observed, changes in the thermodynamic quality of the solvent resulting from the increase in temperature seem to be not substantial.

The temperature affects also both the specific surface area and the pore volume (Figure 2). The specific surface area, determined by the BET technique, is mostly related to the small pores that are not observed in the pore size distribution curves. Because the monomers are thermodynamically better solvating agents for the polymer than the porogen, the precipitated insoluble gel-like nuclei swell with the monomers that are still present in the surrounding liquid. Following the nucleation step, the polymerization continues both within the separated phase of monomer swollen nuclei and in the remaining liquid polymerization mixture. If the polymerization temperature is low, the polymerization rate is slow and transfer of a substantial part of monomers from solution in the nuclei can occur. Polymerization within the nuclei is kinetically preferred because the local concentration of the monomers is higher than in the surrounding solution. As the temperature increases, the number of polymer molecules that are formed in the solution after the original nucleation grows. These are captured by the growing nuclei and form larger clusters with less individualized texture, and the surface area decreases.

At even higher temperature, the polymerization reaction is very fast and more growing chains are transformed into individual globules rather than being captured by the primary nuclei. These globules are small and, therefore, their surface is larger. In contrast to the specific surface area, the changes in total pore volume are small and vary only from 1.33 to 1.50 mL/g in the temperature range 60–90 °C. Obviously, the fraction of voids within the final porous polymer (macropores) is close to the volume fraction of the porogenic solvent in the initial polymerization mixture because the porogen remains trapped in the voids of the cross-linked polymer.

Suspension Polymerization. The polymerization process that occurs in suspension system is simply considered to be a bulk polymerization on a small scale (e.g., refs 13 and 14). We have recently demonstrated that this is not always the case. The true bulk process in a mold differs both because there is no interfacial tension between aqueous and organic phases and because there are no dynamic forces of the type found in a stirred suspension polymerization.[12] However, the basic mechanism of nucleation applies to both bulk and suspension polymerizations. Therefore, the effect of temperature in the suspension system has to be similar to that described above. Indeed, Figures 3 and 4 show that the distribution profiles for the porous beads obtained from glycidyl methacrylate and ethylene dimethacrylate or diethylene glycol dimethacrylate are shifted toward

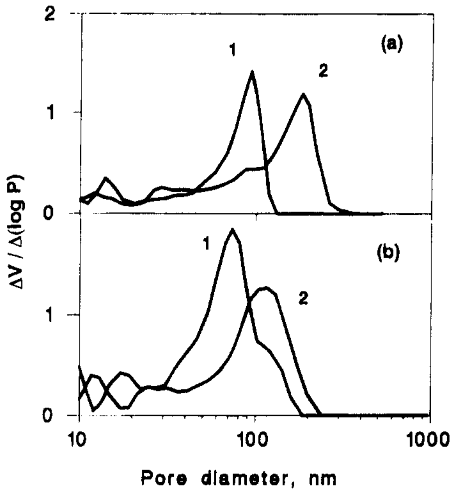

Figure 4. Differential pore size distribution curves of the poly(glycidyl methacrylate-*co*-diethylene glycol dimethacrylate) beads prepared by a suspension polymerization at a temperature of 90 (1) and 70 °C (2) initiated by benzoyl peroxide (a) and azobis(isobutyronitrile) (b).

smaller pore sizes if the polymerization proceeds at a higher temperature. Figure 4 also shows the effect of the type of initiator used for the polymerization. In general, polymerizations initiated by benzoyl peroxide provide beads with larger pores than AIBN. This correlates well with the decomposition rates of these initiators: benzoyl peroxide is slower than AIBN by a factor of about 4.[15] Slower initiation results in a slower polymerization rate and therefore in conditions that are more advantageous for the diffusion of monomers and the formation of larger globules.

Conclusion. Our experimental results show that the temperature is the most convenient variable to adjust the pore size distribution of macroporous media because it does not require any change in the composition of the reaction mixture.

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