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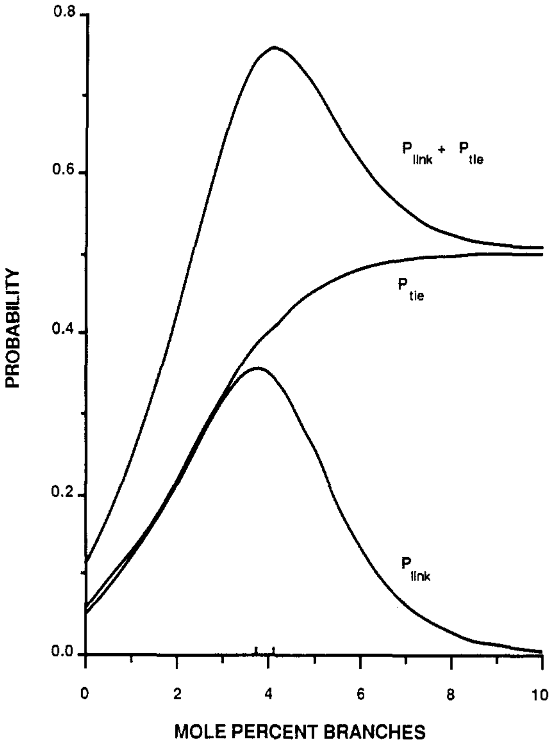

Figure 1. Probabilities of physical and topological intercrystalline connections calculated from the model with input parameters W_a = 150 Å and W_c = 90 Å. P_{link} attains a maximum at p = 3.75%. $P_{tie} + P_{link}$ attains a maximum at p = 4.1%.

made recently. The maxima are caused by two conflicting effects of reluctance of the side chains to enter the crystal structure. On one hand, longer amorphous loops are produced, thus tending to increase the liklihood of linking for a given pair of opposing loops. On the other hand, heavier amorphous loops are produced, so at constant density there are fewer opposing pairs.

Discussion. The maximum values at around 4% branching illustrated in Figure 1 occur where substantial morphological change has been observed in the laboratory[7] and may have a role in explaining this as well as changes in certain mechanical properties as functions of branch content.[4,5] Two ameliorating points must be kept in mind, however. First, the fixed input parameters W_a and W_c represent only a hypothetical copolymer series as p varies. In practice, W_c varies from around 150 Å to a floor of 50 Å (for ethylene–1-alkenes) as p increases from 0 to around 4%, while W_a varies in the opposite direction.[7] For p exceeding 5%, the crystalline state becomes increasingly difficult to observe. Second, there is evidence that the increases in tie and link probability for small p are accompanied by increases in the number of interphase loops and decreases in the number of completely amorphous subchains. Any quantitative study of tight or small-reach loops must take into account variation in interphase content, a phenomenon not considered in the present computations. A thorough study, taking into account experimentally determined variation in amorphous, interphase, and crystal dimensions as functions of p, may produce substantial indirect evidence as to the extent to which topological linking occurs between amorphous loops and what influence these links have on morphological and mechanical properties.

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Registry No. Ethylene, 74-85-1.

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R. C. Lacher*
Department of Computer Science
Florida State University
Tallahassee, Florida 32306

J. L. Bryant
Department of Mathematics, Florida State University
Tallahassee, Florida 32306

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Vitrification of Water in a Hydrogel

Polymers prepared from 2-hydroxyethyl methacrylate (PHEMA) imbibe about 43 wt % water at equilibrium and, in this respect, are rather insensitive to inclusion of cross-linking comonomers, such as dimethacrylates.[1] A number of techniques have been used to investigate these PHEMA hydrogels[2-7] and distinctions made about the environment of water molecules, using such adjectives as "bulk", "bound", and "interfacial".[6] Dynamic mechanical analysis (DMA), using torsion pendulums,[8-12] revealed a γ-transition in dry PHEMA, near −131 °C (1 Hz),[12] which was attributed to side-chain motion.[8] As water content was increased, the γ-transition was gradually replaced by a β-transition, which varied from −77 to −109 °C (1 Hz).[12] As is customary in DMA work,[13] the value of a transition was taken as the maximum of the mechanical loss (tan δ). In the present work an alternative approach is pursued[14,15] according to which a transition temperature is assigned by reference to changes in the modulus of elasticity (E'). In a preliminary report, this approach resulted in discernment of a vitrification process with a glass transition temperature, T_g, similar to values reported for water.[16]

Homogeneous solutions of HEMA (3.0 mL), triethylene glycol dimethacrylate (0.6 mL), both from Aldrich, and distilled water (2.2 mL) were exposed in glass molds to γ-rays from a ^{137}Cs source: dose rate = 0.8 Mrad/h; dose = 4.8 Mrad; ambient temperature = 40 °C. The highly cross-linked hydrogel products were soft and transparent; they contained little residual monomer. After prolonged equilibration in distilled water, the water content of the hydrogels was 40–43 wt %. For comparison, similar specimens were made with glycerol in place of water. This was done at the maximal solubility of glycerol in the mo-

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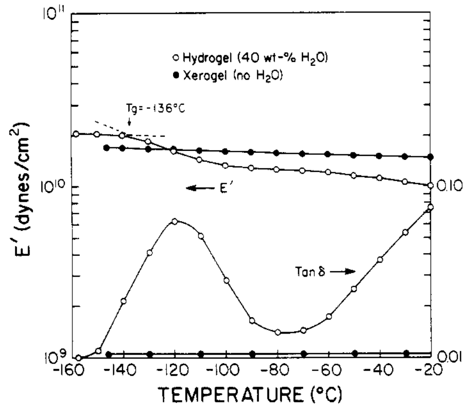

Figure 1. Dynamic mechanical spectra (*E'*, tan δ) of cross-linked poly(2-hydroxyethyl methacrylate) xerogel and hydrogel.

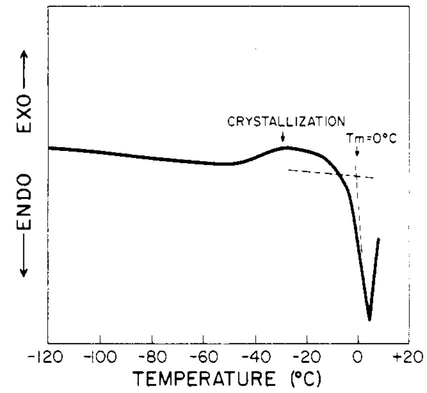

Figure 2. Thermogram (DSC) of the hydrogel.

nomer mixture, i.e., 20%. Specimens (6.0 cm × 0.4 cm × 0.05 cm) were cooled with liquid nitrogen and subjected to a sinusoidal tensile strain, at 11 Hz, using an Autovibron apparatus (IMASS, Hingham, MA). *E'* and tan δ were monitored automatically as the temperature was raised by 2.5 °C/min. Other samples were examined by differential scanning calorimetry (DSC) at 10 °C/min (Du Pont 990 thermal analyzer).

Dynamic mechanical analysis (DMA) results are shown confined to low temperatures at which artifacts due to evaporation of water from the hydrogels are negligible (Figure 1). The decrease in *E'* is consistent with a transition from a glassy state. The onset of the transition is defined by reference to *E'*, as shown by the arrowhead in Figure 1. In other work on highly cross-linked polymers, this preference was justified on the grounds that it gives much better agreement with the classical method of assigning T_g by reference to coefficients of thermal expansion.[14,15] The transition begins at −136 ± 3 °C and is attributed to devitrification of water. Comparison of the above value with extrapolated DSC data for aqueous solutions which could be vitrified shows excellent agreement, i.e., T_g for water by DSC is −137 ± 1 °C.[17]

The DSC apparatus available was not suitable for detecting transitions at sufficiently low temperatures to study devitrification of water. However, on warming through higher temperatures evidence that devitrification resulted in formation of a liquid was obtained on samples which had been cooled as in the DMA experiments (Figure 2). There is an evolution of heat beginning near −40 °C which is close to the minimum temperature to which, normally, water can be undercooled without ice formation.[18] There is evidence that undercooling of water is favored by the presence of polyhydroxy compounds[19] and by proximity to various surfaces.[20]

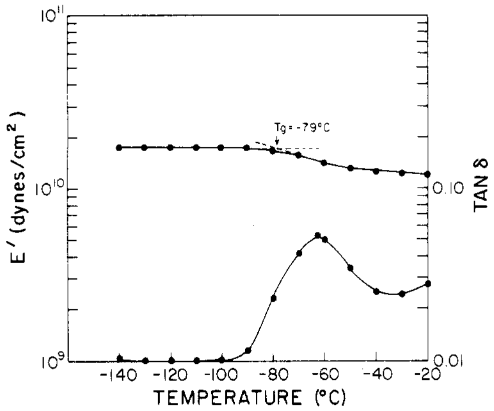

Figure 3. Dynamic mechanical spectra (*E'*, tan δ) of glycerol-saturated gel.

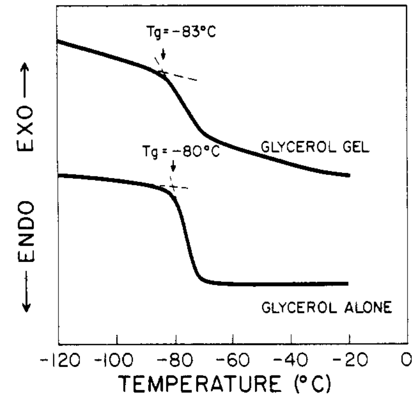

Figure 4. Thermogram (DSC) of glycerol alone and glycerol-saturated gel.

The main evidence presented here for vitrification of water depends on the appropriate assignment of a value of T_g for water. In order to test the validity of the procedures used, similar experiments were made with glycerol, in place of water, as the exemplar of a liquid which is readily vitrified.[21] Satisfactory agreement was obtained from values of T_g derived for data on gels by both DMA (T_g = −79 °C; Figure 3) and DSC (T_g = −83 °C; Figure 4): glycerol alone gave, by DSC, T_g = −80 °C; Figure 4.

In broader perspective a low-temperature glass transition has also been reported in hydrated proteins by reference to modulus of elasticity data obtained by DMA. The transition was attributed to "immobilization of the protein groups with strongly bound water".[22] When analyzed from the present point of view the data indicate an involvement of water vitrification beginning near −137 °C. Thus an underlying question raised by the work on both PHEMA and proteins is the nature of the microenvironment in which a limited number of "interfacial" water molecules appear to give a T_g, near −137 °C.

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Registry No. (HEMA)(triethylene glycol dimethacrylate) (copolymer), 62083-88-9; H_2O, 7732-18-5.

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T. W. Wilson and D. T. Turner*

Dental Research Center and Department of
Operative Dentistry, University of North Carolina
Chapel Hill, North Carolina 27599-7455

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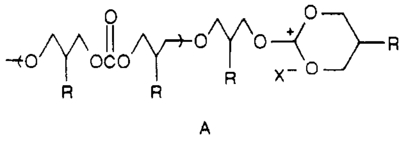
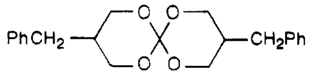
Polymerization and Block Copolymerization Initiated by Unusually Stable Living Propagating Species Formed in the Cationic Polymerization of Spiro Ortho Carbonate[1]

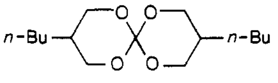
Current interest in the area of polymer synthesis has been directed to the living polymerization based on the stable propagating end species. This offers the crucial synthetic method for polymers of controlled molecular weights. Living cationic,[2] anionic,[3] coordination,[4] radical,[5] and group-transfer[6] polymerizations are of recent advances in this field. Meanwhile, the cationic polymerization of spiro ortho carbonate (SOC) forming a polyether–carbonate alternative copolymer is believed to proceed via trialkoxycarbenium ion (A) as a possible propagating species.[7] Since this type of carbenium ion is well-known to be quite stable as reported by Olah et al.,[8] this growing end (A) should still remain living after the completion of the polymerization. We have confirmed the special stability of the end species and now disclose the preliminary results on it.



A



SOC 1



SOC 2

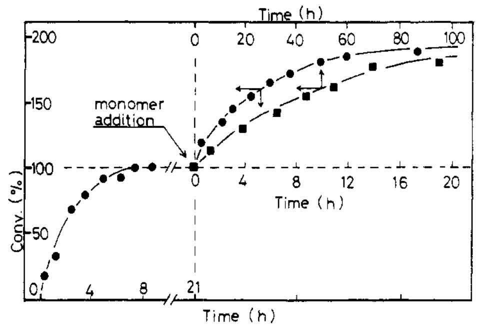


Figure 1. Time–conversion curves of the cationic polymerization of SOC 1 with $Ph_3C^+BF_4^-$ in chlorobenzene at room temperature.[10] At the first stage (0–21 h) SOC 1 was polymerized completely within 9 h (●). At the second stage, fresh SOC 1 dissolved in the solvent (in the same concentration) added to the poly(SOC 1) solution was consumed within ca. 30 h (●), while it took ca. 120 h to consume fresh SOC 1 added to the poly(SOC 1) solution after heating at 120 °C for 2 h (■).

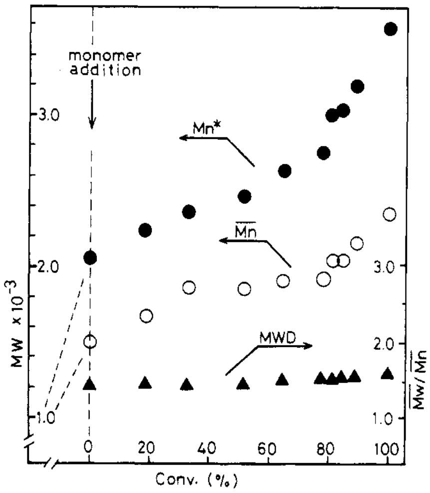


Figure 2. Molecular weight $\overline{M}_n$ (○), M^* (●), value of peak top in GPC), and MWD (▲) of the poly(SOC 1) at the second stage, obtained with $Ph_3C^+BF_4^-$ in chlorobenzene at room temperature, as a function of monomer conversion.

Cationic polymerization of SOC 1 with $Ph_3C^+BF_4^-$ or BF_3OEt_2 was found to proceed at room temperature (RT).[9] Time–conversion of the polymerization was obtained by ^1H NMR work (Figure 1).[10] To our surprise, after the complete consumption of SOC 1, the polymerization clearly took place again when the same amount of fresh SOC 1 was introduced to the reaction system (Figure 1). The added monomer was consumed thoroughly in 30 h in the second stage. Furthermore, fresh SOC 1 added to the living poly(SOC 1) solution, which was obtained by heating at 120 °C for 2 h after the complete polymerization at the first stage, was consumed similarly, though the rate decreased (Figure 1). This supports strongly the presence of a stable and long-lived propagating end of the poly(SOC 1).

As shown in Figure 2,[11] $\overline{M}_n$ and M^* (peak top value) of the sample withdrawn from the polymerization solution of the second stage undoubtedly increased roughly in proportion to the monomer conversion. MWD ($\overline{M}_w/\overline{M}_n$) was not narrow but approximately constant (1.45–1.61) during the polymerization.

On the other hand, block copolymerization was carried out with another SOC 2, which was added after the complete consumption of SOC 1.[12] The initial poly(SOC 1)

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