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# Intra and intermolecular relaxations 2,3-dihydroxypropyl methacrylate and 2-hydroxyethyl methacrylate hydrogels

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## Abstract

The dynamic mechanical transitions present in the 2-hydroxyethyl methacrylate (HEMA) and 2,3-dihydroxypropyl methacrylate (DHPMA) homopolymers and two random copolymers, with one-to-one and three-to-one HEMA-to-DHPMA molar ratios, were examined by analyzing the dry xerogels and hydrogels at various states of hydration. The temperatures of the primary $\alpha$ transition and the secondary $\beta$ and $\gamma$ transitions were determined in the tension mode; the storage modulus and loss modulus as a function of temperature and frequency were recorded. The results were compared to the results obtained from dielectric analysis at low hydration using tan $\delta$. The frequency dependence of the dispersions was calculated for the dry and hydrated states, using mechanical and dielectric data. The information obtained was used to elucidate the interaction between the polymer and the sorbed water. Analysis of the low temperature secondary $\gamma$ transition and secondary transitions resulting from polymer–water interactions was emphasized. During the initial hydration, the temperature maxima of the dielectric and mechanical secondary $\gamma$ transitions, and the transitions that appear in the presence of absorbed water increased as the DHPMA content increased. The apparent activation energy associated with the secondary transitions increased as well. All of this is the result of stronger intermolecular interactions due to the increased density of hydrophilic moieties in DHPMA.

*Keywords:* Hydrophilic polymer; Intermolecular relaxation; Secondary transition

## 1. Introduction

Relaxation and transport behavior in poly (2-hydroxy ethyl methacrylate) (PHEMA) have been extensively studied. However, there is a paucity of data in the literature on the characterization of poly (2,3-dihydroxy propyl methacrylate), also referred to a poly (glyceryl methacrylate). Recent innovations in DHPMA purification techniques have lead to the availability of material for study [1]. The syntheses of novel hydrogels composed of cross-linked DHPMA homopolymer and cross-linked DHPMA/HEMA copolymers have generated much interest in their use as contact lens materials and in other biomedical applications. This interest stems from the fact that the equilibrium water content (EWC) increases with DHPMA content. For a series of polymers at constant cross-link concentrations the EWCs varied from 38% for HEMA homopolymer to 75% for DHPMA homopolymer. To date research characterizing these polymers is limited. In one study, differential scanning calorimetry (DSC) was used to define water structure in DHPMA homo and copolymers [2]. Water is classified as free water (freezing) or bound water; bound water is further divided into freezing bound water and non-freezing bound water [3]. Increasing the DHPMA content increased the freezing, freezing bound and non-freezing water content in copolymers as compared to HEMA. DHPMA homopolymer contained free and non-freezing bound water, but no freezing bound water [2]. McConville and Pope [4] used the pulsed field gradient NMR method to characterize bound water in these copolymers. They concluded that bound water determined via the NMR study agreed with the amount of non-freezing water measured on similar materials using DSC. In another study using NMR proton $T_2$ relaxation time measurements they demonstrated that motional correlation times are related to the average mobilities of water molecules and polymer chains [5].

These and other hydrogels are hydrophilic polymer

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Table 1
Characterization information for materials studied

| Polymer name | Molar ratio DHPMA/HEMA | Lot number | Deionized water content at 23 °C (wt%) | Linear expansion coefficient |
|---|---|---|---|---|
| DHPMA | 1:0 | 49002G15X | 75 | 1.59 |
| 1 DHPMA/1 HEMA copolymer | 1:1 | 937105G5X | 59 | 1.39 |
| 1 DHPMA/3 HEMA copolymer | 1:3 | 841088G3X | 49 | 1.28 |
| HEMA | 0:1 | 802522PMCL | 38 | 1.19 |

networks that can imbibe large quantities of water without dissolving. Cross-linked HEMA polymers and DHPMA polymers are biologically compatible hydrogels particularly useful in ophthalmology and pharmacy. For applications such as contact lenses, the importance of the dynamic mechanical analysis (DMA) of hydrogels cannot be overestimated, since DMA mimics the cyclic loads of differing magnitudes involved in wear [6]. In the examination of swelling-controlled release systems for drug delivery, the bulk, dynamic properties of hydrogels can be measured by DMA [7]. Although the mechanical and dielectric behavior of HEMA has been studied extensively, corresponding studies of DHPMA are absent; therefore, HEMA relaxation spectra serve as a reference for this study of DHPMA.

Below the primary glassy-to-rubbery transition temperature, $T_g$, the secondary relaxations that occur in glassy polymers above the temperature of liquid nitrogen have been tentatively divided into four types [8]. These four classes are: motion of short chain segments of the main polymer chain, (i.e. polyvinyl chloride, polysulphones); rotation of a side group attached to the main polymer chain, (i.e. polymethyl methacrylate, polymethyl acrylate); internal motion within the side group itself, (i.e. motion in R of the –COOR group in polyalkyl methacrylates); and motion of, or taking place within, a small molecule dissolved in the polymer, (i.e. the *n*-butyl group in dibutyl phthalate). In HEMA, the β transition has been attributed to the second type of motion, rotation of the ester side group [9,10]. The γ transition in HEMA has been attributed to the third type of motion; rotation of the hydroxyethyl group attached to the ester moiety. Upon hydration in HEMA, a new secondary transition forms, the $\beta_{sw}$ transition, at temperatures slightly greater than the original γ transition; the new transition has been attributed to water molecules interacting with the hydroxyalkyl group on the polymer side chain and represents the third type of motion previously described. DMA results were compared to data obtained from dielectric analysis of DHPMA to determine the effect of ethylene glycol versus glycerol esters on relaxation behavior.

## 2. Experimental

### 2.1. Materials

Four cross-linked polymers, supplied as soft contact lens blanks of standard size, (12.8 mm diameter, 6.0 mm thick), were manufactured by and obtained from Benz Research and Development Corporation, located in Sarasota, FL: the HEMA and DHPMA homopolymers, and two HEMA/DHPMA copolymers. The names and compositions of the polymers, lot numbers, and the weight-percent water content at equilibrium are in Table 1. All the materials were bulk polymerized via an azo, free radical initiator by a patented process [11] with water or ethylene glycol used as a diluent during synthesis; the cross-linker concentration was approximately 0.2% by weight ethylene glycol dimethacrylate.

### 2.2. Sample preparation

For DMA analysis, the 12.6 mm diameter, 8 mm thick contact lens blanks received from the manufacturer were cross-sectioned to 1 mm thick disks using a diamond saw lubricated with silicone oil. The 1 mm thin disks were first thoroughly rinsed in hexanes, (Aldrich, ACS grade), dried in the atmosphere, completely hydrated three times in deionized water, cut to a rectangular shape, and finally, oven dried for 3–6 h. The dimensions of the samples for DMA analysis were approximately 10 mm long, 1 mm thick and 6 mm wide. A minimum 10:1 length to thickness ratio was maintained. The oven-drying period, at 120 °C under vacuum, was longer for the samples containing more DHPMA. After the oven-drying period, samples were stored in a dessicator over $P_2O_5$ for 24 h. The absolute polymer mass was determined gravimetrically, to ± 0.01 mg, only after further drying produced no change in the sample mass. After DMA data was collected for the xerogel, the samples were swelled to equilibrium in water. To achieve the different water content, the swelled samples were dried for different short periods of time and sealed in airtight containers for an equilibration period of 1 week. The weight-percent water content was determined immediately prior to DMA analysis, based on the dry polymer mass and the hydrated mass; this was converted to mole fraction based on the molecular mass of the mer.

A technique developed by Malmstrom et al. was used to prepare samples for dielectric analysis [12,13]. This technique has been proven useful for samples, which cannot be heat or solvent processed into pinhole free films. Cross-linked lens blanks cannot be hot-pressed into 30 mm into the diameter disks required for the dielectric analysis

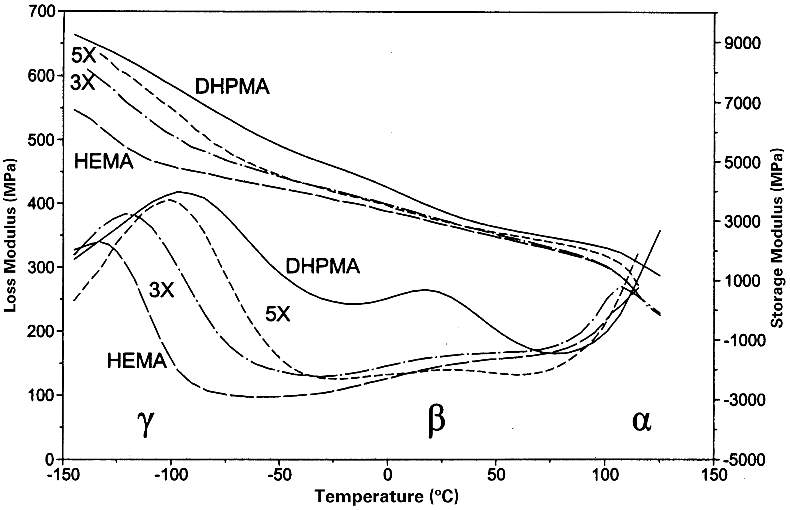

Fig. 1. The loss modulus and the storage modulus data for the four dry xerogels at 1 Hz.

experimental apparatus. Therefore, Malmstrom's technique was used to produce cross-linked polymer/polyethylene composite films. The swelled thin disks cut from the contact lens blanks were dried and ground to a fine powder. The powder was sandwiched between two thin sheets of polyethylene (Marlex 6000) and pressed together at 130 °C using a hydraulic press. A disk was cut from the composite for dielectric analysis. Xerogel composites and hydrogel composites sorbed to increasing hydration states under ambient humidity and temperature conditions were examined. Using this sample preparation technique, accurate transition temperatures and activation energies are obtained via DEA.

### 2.3. Instrumentation

The T.A. Instruments Dynamic Mechanical Analyzer 2980, was used in the tension mode to obtain the reported mechanical data. T.A. Instruments *Thermal Advantage* software was used to operate the instrument, and the program, *Universal Analysis* 2.6, was used for data processing and presentation. The temperature range of each analysis was from − 145 to 140 °C, achieved using the T.A. Instruments nitrogen gas cooling accessory, (GCA). The frequency range of each analysis was from 0.5 to 30 Hz, and the amplitude was 3 μm. The method used for each DMA analysis consisted of three steps: a 3-minute isothermal step, a frequency sweep, and a 5 °C temperature-increment step. A preload force of 0.001N was used to maintain sample tension, and the force tracking option was used at 105%. The apparent activation energy for each secondary transition was calculated from Arrhenius dependence, and the results are presented in kcal/mol in order to be consistent with previous hydrogel studies that are published in the scientific literature. No attempt was made to prevent dehydration of the polymers during the DMA analysis, since dehydration was not observed at low water content, $<0.4$-mole fraction. Dehydration was recorded for samples containing $>0.4$-mole fraction water, but only at temperatures greater than 25 °C, so that only the analysis of the high temperature α transition as a function of water content was prevented.

Dielectric analysis was conducted using the T.A. Instruments Dielectric Analyzer 2820, equipped with parallel plate sensors and nitrogen gas purge. The TA Instruments software previously described was used to acquire and process data. The temperature range of each analysis was from − 150 to 140 °C; this was achieved using the T.A. Instruments liquid nitrogen-cooling accessory, (LNCA). The frequency range of each analysis was from 0.1 Hz to 100 kHz. Prior to data collection, the sample was compressed at 120 °C under an applied force of 250N to ensure good sensor contact. The method used for each analysis consisted of three steps: a 3-minute isothermal step, a frequency sweep, and a 5 °C temperature-increment step.

## 3. Results and discussion

### 3.1. The dry xerogels

The dry HEMA and DHPMA homopolymers and the copolymer xerogels, 1 DHPMA/3 HEMA copolymer and 1 DHPMA/1 HEMA copolymer, all exhibited three viscoelastic mechanical transitions, named α, β, and γ according to decreasing temperature; the xerogel mechanical transitions are presented in the loss modulus and the storage modulus data in Fig. 1 at 1 Hz. The temperatures of all the xerogel and hydrogel mechanical dispersions at 1 Hz are summarized in four Fig. 2A–D for HEMA, 1 DHPMA/3 HEMA copolymer, 1 DHPMA/1 HEMA copolymer and DHPMA, respectively. Reproducible DMA data through $T_g$ were not obtained for low water contents because the

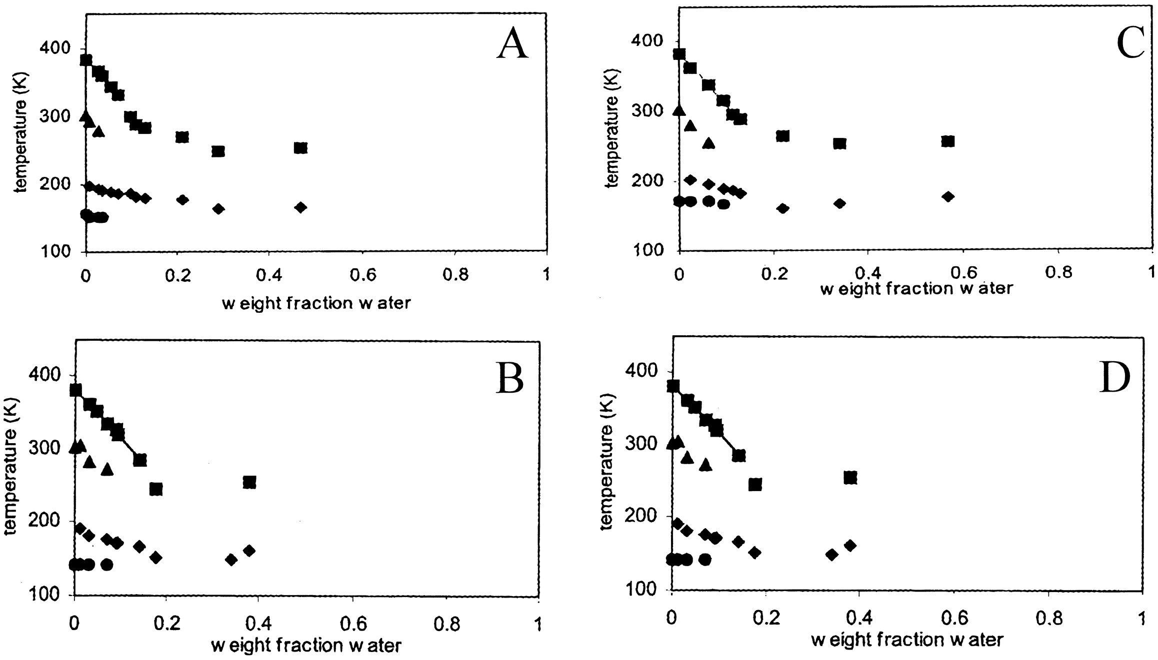

Fig. 2. A summary of the loss modulus temperature maxima from the DMA transitions at 1 Hz for the HEMA homopolymer during hydration: (■) represents the α transition or $T_g$, (▲) represents the beta transition, (◇) represents the $\beta_{sw}$ transition, and (•) represents the γ transition, (A) HEMA; (B) 1 DHPMA/1 HEMA; (C) 1 DHPMA/1 HEMA; (D) DHPMA.

materials became too soft during the 5 °C increment method step.

As with most amorphous vinyl polymers, the high temperature α transition was attributed to the onset of large scale, cooperative displacements of the methylene chains in the macromolecular network, and represents the glassy-to-rubbery transition temperature, or the $T_g$ [7,14–16]. The high temperature α transition for these four xerogels was the same, 105 °C, as indicated by the onset point for the $T_g$ in the storage modulus data in Fig. 1 and summarized in Fig. 2. DSC results of the glass-transition temperature previously reported for these xerogels using 5 °C/min heating rate were approximately 5 °C greater than the onset point for the glass-transition derived from DMA storage modulus results [2]. The temperature of the α transition was greatly affected by the oven-drying period under vacuum. The HEMA homopolymer required four hours and the DHPMA homopolymer required eight hours to achieve a constant weight and reproducible DMA results for all three xerogel transition temperatures. Longer drying times for the DHPMA homopolymer resulted in yellowing of the sample, indicating thermal degradation.

The β transition in methacrylates was attributed to the onset of partial rotation of the pendant, ester moiety [8]. The three xerogels containing DHPMA exhibited a β transition at approximately the same temperature as the HEMA xerogel, about 28 °C, as indicated in the loss modulus data at 1 Hz in Fig. 1 and summarized in Fig. 2. This transition was most pronounced in the DHPMA xerogel, and the apparent activation energy was 32 kcal/mol, determined from the loss modulus temperature maxima Arrhenius dependence. The frequency dependence for the other three xerogels was not possible because the β transition merged with the high temperature α transition at frequencies greater than 3 Hz. Extensive studies have shown that poly (*n*-alkyl methacrylates) exhibit α and β relaxations that merge into a single process termed the αβ process. The extent of merging is related to the effect of cooperative α process on the β relaxation process [17–20]. Using a frequency of 1 Hz, the HEMA xerogel was reported to have a higher β transition temperature, 27 °C, (compared to other poly (alkyl methacrylates) with a β transition at 7 °C and chloro derivatives of poly (ethyl methacrylate) with a β transition at 0 °C, due to higher polarity and stronger interactions of the side chains [10]. The increased height and area of the β transition in DHPMA suggests greater extent of the dissipative mechanism, compared to HEMA [21].

A low temperature γ transition was clearly resolved for all four xerogels, and this was attributed to motion of the hydroxyalkyl moieties attached to the ester side chain, as previously established for the HEMA xerogel [9]. Some previously reported DMA data for HEMA showed the absence of this transition in the xerogel at temperatures above − 160 °C using similar frequencies [22]. The temperature of the dry γ dispersion increased as the amount of DHPMA increased, from − 132 °C in HEMA to − 96 °C in the DHPMA homopolymer, as presented in Fig. 1. The increased temperature for the γ transition reflects greater interaction between hydroxyalkyl groups on the side chains in the xerogel as the DHPMA content is increased. This was corroborated by the increasing apparent activation energy calculated from the Arrhenius dependence of the loss

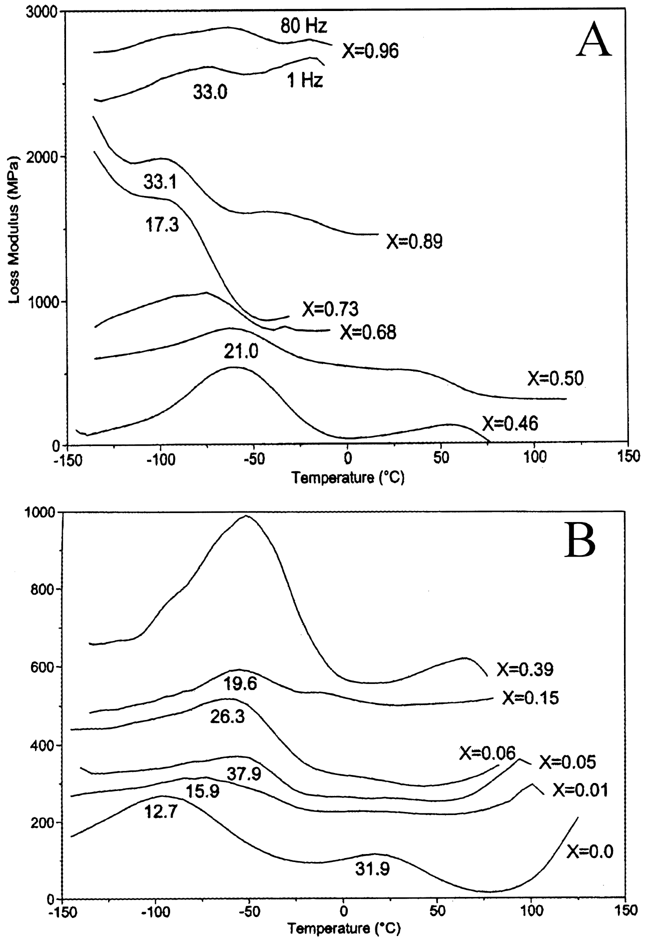

Fig. 3. Loss modulus data at 1 Hz for the DHPMA homopolymer hydrogel at high (A) and low (B) hydration states. The water mole fraction (X = ) is indicated at the right of each curve, and the apparent activation energy (kcal/mol) is indicated beneath each transition. The 80 Hz scan at high hydration is included for comparison.

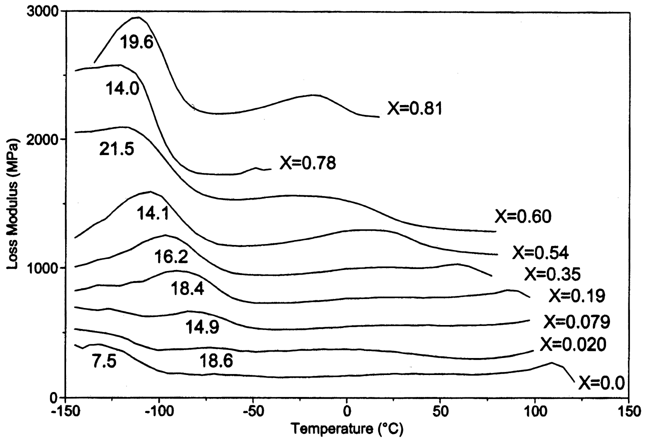

Fig. 4. Loss modulus data at 1 Hz for the HEMA hydrogel during hydration from the dry state to the completely hydrated state. The water mole fraction (X = ) is indicated at the right of each curve, and the apparent activation energy (kcal/mol) is indicated beneath each transition.

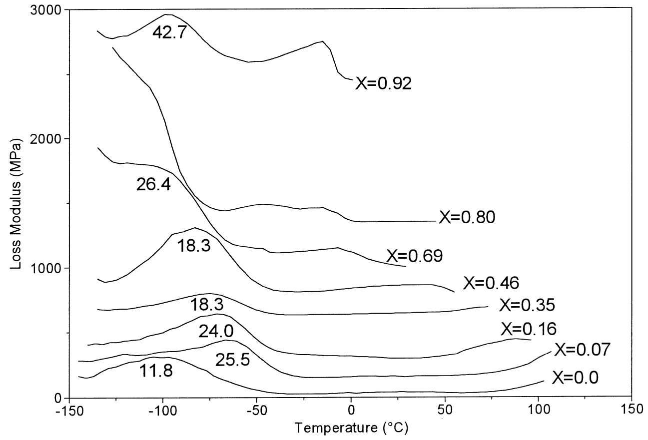

Fig. 5. Loss modulus data at 1 Hz for the 1 DHPMA/1 HEMA copolymer hydrogel during hydration from the dry state to the completely hydrated state. The water mole fraction (X = ) is indicated at the right of each curve, and the apparent activation energy (kcal/mol) is indicated beneath each transition.

modulus maxima. For the HEMA, 1 DHPMA/3 HEMA copolymer, 1 DHPMA/1 HEMA copolymer and DHPMA xerogels, the apparent activation energy was 7.5, 11.5, 11.8, and 12.7 kcal/mol, respectively, for the γ transition. Interestingly, the apparent activation energy for the γ transition in the DHPMA xerogel was almost double that observed in HEMA and there are double the number of hydroxyl groups on each side chain in DHPMA. In addition, at temperatures below the γ transition temperature, the storage modulus increased as the DHPMA content increased, indicating greater side chain interaction at the low temperature limit of the analysis.

The effect of hydration on the mechanical dispersions in all four materials was qualitatively similar, as depicted in the loss modulus data at 1 Hz, presented in Figs. 3–6, respectively, for DHPMA (high [A] and low [3B] water content), HEMA, 1 DHPMA/1 HEMA copolymer and 1

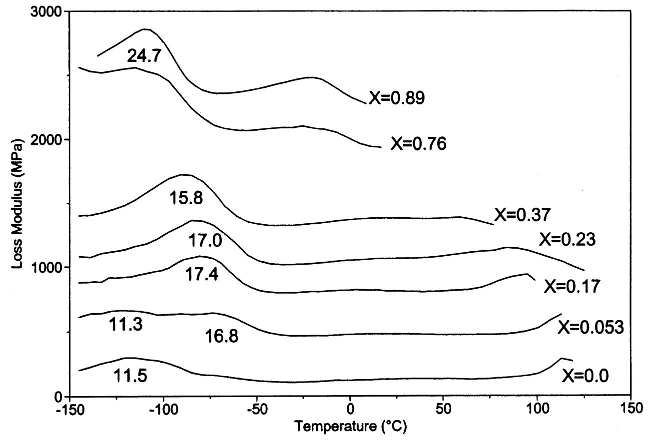

Fig. 6. Loss modulus data at 1 Hz for the 1 DHPMA/3 HEMA copolymer hydrogel during hydration from the dry state to the completely hydrated state. The water mole fraction (X = ) is indicated at the right of each curve, and the apparent activation energy (kcal/mol) is indicated beneath each transition.

DHPMA/3 HEMA copolymer. The temperature of the α transition decreased as the xerogels imbibed water; therefore, water plasticized the polymer matrix. At high water content, the high temperature α transition was never observed below approximately −25 °C, due to the formation of a water phase. This was confirmed using DSC, and reflects the composite nature of the highly swollen hydrogels [2]. As the α transition temperature decreased, it merged with the β transition. This obscured the temperature position and frequency dependence for the β transition during hydration in all the materials studied, except for the DHPMA homopolymer. The β transition maximum in the DHPMA xerogel loss modulus data at 1 Hz occurred at 29 °C but increased to 32 °C with a water content of 4.7 mol%; the intensity remained relatively constant. At 6.1 mol% water content, the β transition temperature decreased, to 21 °C, and the intensity decreased. A similar phenomenon was reported for the dry β transition as water was imbibed by HEMA during mechanical deformation in shear, but since the dry β transition merged with the α transition upon hydration, this was not confirmed for HEMA during this investigation [9]. In DHPMA at 0.15 mole fraction water, the β transition temperature maximum occurred at approximately −10 °C, but at 0.39 mole fraction water, the β transition merged with the low temperature transition.

Upon initial hydration, the intensity of the low temperature γ transition in all the xerogels gradually decreased while the temperature remained constant, as indicated in the loss modulus data in Figs. 3–6. Simultaneously, a new dispersion, named the $\beta_{sw}$ transition, formed at temperatures greater than the original γ transition but less than the β transition exhibited by the xerogel. The $\beta_{sw}$ transition decreased in temperature during hydration until a low temperature limit was achieved, and increased in intensity at the expense of the γ transition observed in the xerogel. The transformation of the γ mechanical transition into the $\beta_{sw}$ mechanical transition was reported previously for HEMA, poly (5-hydroxy-3-oxapentyl methacrylate), poly (*n*-propyl methacrylate) and poly (2-hydroxyethyl acrylate) swollen with water, ethylene glycol and other polar solvents [9,21]. In this study of HEMA, there was no evidence of the original γ transition at 0.35-mole fraction water, roughly corresponding to one water molecule for every two –OH groups on two HEMA side chains, as was noted previously [9]. However, in DHPMA, the original γ transition disappeared at slightly greater water content, 0.46-mole fraction water. During subsequent hydration, the intensity of the $\beta_{sw}$ transition decreased at constant temperature. The $\beta_{sw}$ transition was not depressed to temperatures lower than that observed for the xerogel γ transition. Finally, at very high water content approaching the equilibrium value, the intensity of the $\beta_{sw}$ transition increased, while the temperature increased slightly in all the hydrogels. To explain the molecular origin of the $\beta_{sw}$ transition in HEMA, it was proposed that two lateral hydroxyethyl side groups, linked by one water molecule during initial hydration, create the $\beta_{sw}$ transition at temperatures greater than that observed for the xerogel γ transition as a result of water molecules hindering partially side group rotation [9]. Although the mechanical data from the analysis of DHPMA hydrogels cannot confirm this hypothesis, the results were consistent with this interpretation.

From the Arrhenius dependence of the loss modulus temperature maxima, the apparent activation energy was calculated for the $\beta_{sw}$ transition during hydration in all of the polymers. The apparent activation energy decreased during the initial formation of the $\beta_{sw}$ transition, and the apparent activation energy for the γ transition remained constant. In DHPMA for example, the $\beta_{sw}$ transition first appeared at 0.047 mole fraction water with apparent activation energy of 38 kcal/mol, but decreased to 26 kcal/mol at 0.061 mole fraction water and to 19.6 kcal/mol at 0.15 mole fraction water. Between 0.1 and 0.5 mole fraction water, or at water fractions with some evidence of the original γ transition, the apparent activation remained relatively constant, at approximately 20, 18, 17, 16 kcal/mol for DHPMA, 1 DHPMA/1 HEMA copolymer, 1 DHPMA/3 HEMA copolymer and HEMA, respectively. The apparent activation energy increased by approximately 5 kcal/mol at mole fraction water $0.5 < X < 0.7$; greater mole fraction of water, $0.7 < X < 0.8$, decreased the apparent activation energy. Finally, the apparent activation energy substantially increased at the EWC. The changes in apparent activation energy follow the trend established by the changes in the $\beta_{sw}$ transition loss modulus temperature maxima at 1 Hz.

Using a plot of the temperature of the $\beta_{sw}$ transition as a function of weight-percent water content, presented in Fig. 2, it was possible to extrapolate the temperature of the $\beta_{sw}$ transition in the xerogel; these temperatures are −72, −70, −63, and −55 °C for HEMA, 1 DHPMA/3 HEMA copolymer, 1 DHPMA/1 HEMA copolymer, and DHPMA, respectively. The difference between the extrapolated value for the $\beta_{sw}$ transition in the xerogel and the temperature of the γ transition exhibited by the xerogel increased with increasing DHPMA content; the respective differences for HEMA, 1 DHPMA/3 HEMA copolymer, 1 DHPMA/1 HEMA copolymer and DHPMA are approximately 60, 45, 40, and 25 °C.

### *3.2. Results from dielectric analysis*

As mentioned under the sample preparation discussion, dielectric analysis was conducted on the powdered HEMA and DHPMA-containing polymers using a polyethylene composite. The dielectric tan $\delta$ results are presented in Fig. 7A–D, for DHPMA, HEMA, 1 DHPMA/1 HEMA copolymer, 1 DHPMA/3 HEMA copolymer, respectively. Also included are tan $\delta$ plots from DMA at comparable hydration states. The dielectric α transitions were not resolved due to the similarity between

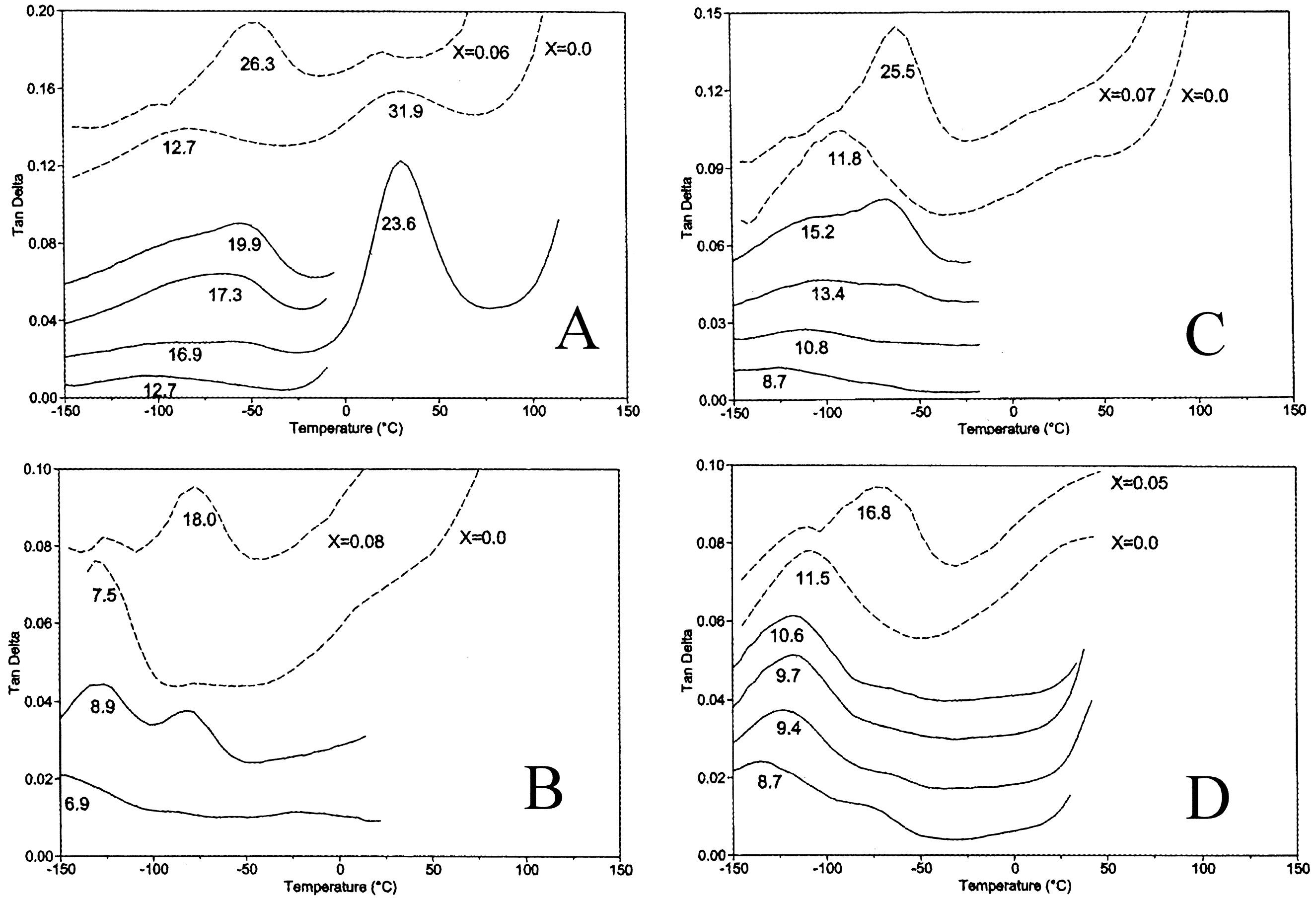

Fig. 7. DMA tan delta (dashed) and DEA tan delta (solid) at 1 Hz. Water mole fraction (X = ) is indicated for the DMA data at the right of each curve; the DEA data is stacked from the xerogel bottom curve in order of increasing hydration states. The apparent activation energy (kcal/mol) is indicated beneath each transition, (A) DHPMA; (B) HEMA; (C) 1 DHPMA/1 HEMA; (D) 1 DHPMA/3 HEMA.

the transition temperatures for the polymers analyzed and the Marlex $T_m$, 120 °C. Cooperative motion between the beta relaxation and alpha relaxation resulted in merged transitions as was noted in the dynamic mechanical data. The dielectric β transition was distinguished from the high temperature α transition only at low frequencies, ≤3 Hz, and only in DHPMA. In the DHPMA sample, the temperature of the dielectric β transition matched the temperature of the mechanical β transition at 1 Hz. The dielectric apparent activation energy for the β transition in DHPMA, 23.6 kcal/mol, was lower than the results from DMA loss modulus data, 31.9 kcal/mol. In other polymer systems, this difference has been attributed to the fact that dielectric dispersions result only from dipole–dipole van der Waals forces, while mechanical deformations contain contributions from both polar and non-polar forces [23]. The low temperature secondary transitions, γ and $\beta_{sw}$, are well resolved. The apparent activation energy of the dielectric γ transition was calculated from the Arrhenius dependence of the dielectric tan δ temperature maxima on frequency from 0.1 Hz to 100 kHz. The transformation of the γ dielectric transition into the $\beta_{sw}$ dielectric transition was reported for poly(hydroxyethyl acrylate) hydrogels [24] and was also noted in DMA data.

The temperature of the γ transition determined mechanically was consistently higher than that measured dielectrically; this was documented previously for HEMA [9]. The temperature maxima of the $\beta_{sw}$ transition measured dielectrically were also slightly lower than the DMA results for all four materials. In the DHPMA homopolymer xerogel, the apparent activation energy for the dielectric γ relaxation is the same as that determined via DMA. However, in HEMA, the corresponding DMA results were slightly higher, 7.5 kcal/mol, than the dielectric results, 6.9 kcal/mol. The apparent activation energy from the dielectric analysis of the γ transition in both copolymer xerogels was 8.7 kcal/mol, compared to 11.5 and 11.8 kcal/mol obtained from DMA. Again this difference noted in the copolymers and in HEMA homopolymer is attributed to non-polar van der Waals forces that contribute to the transfer of mechanical load. It is tempting to speculate that DMA and DEA activation energies for the γ transition in DHPMA homopolymer samples coincide because the contributions from the extra hydroxyl group to the overall van der Waals forces overpower the effect of other secondary forces in transferring mechanical loads. The γ transition behavior of poly (methyl methacrylate) is quite different from that of DHPMA in this respect. That is, non-polar methyl group motion in the ester group is detected by DMA, but not by DEA.

## 4. Conclusions

DMA was conducted on the HEMA and DHPMA homopolymers and the two HEMA/DHPMA copolymers in the dry state and at various water contents during the sorption of deionized water from the dry state to the fully equilibrated state. The influence of water on the mechanical transitions in HEMA was well documented previously, up to approximately half the EWC. The results from this investigation reproduced results previously reported for HEMA at low hydration states, but also provided new information about how the mechanical transitions in HEMA were influenced by high water content, up to and including the equilibrium state. The results from the mechanical analysis of DHPMA homopolymers and copolymers during hydration, from the dry state to the equilibrium state, have not been documented previously. The DMA analysis of HEMA was conducted to establish a foundation for the interpretation of data from the DMA analysis of DHPMA-containing hydrogels. The results from the DMA and DEA analysis of DHPMA provided evidence to support the theory that the intermolecular origins of the transitions that arise during hydration were the result of water molecules linking the hydroxyalkyl side chains in the polymers and hindering partial rotation.

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