

Hydrogels Based on Copolymers of *N*-(2-Hydroxyethyl) methacrylamide, 2-Hydroxyethyl Methacrylate, and 4-*t*-Butyl-2-hydroxycyclohexyl Methacrylate

G. FRIENDS, J. KÜNZLER,* J. MCGEE, and R. OZARK

Bausch and Lomb, Inc., Rochester, New York 14692

SYNOPSIS

A nonionic, high water content, high-strength hydrogel based on *N*-(2-hydroxyethyl) methacrylamide (HMA), 2-hydroxyethyl methacrylate (HEMA), and a strengthening agent, 4-*t*-butyl-2-hydroxycyclohexyl methacrylate (TBCM). The HMA was prepared by the reaction of methacryloyl chloride with ethanol amine. The copolymerization of HMA with varying concentrations of HEMA and TBCM resulted in transparent hydrogel films possessing a wide range of mechanical and physical properties. A copolymer composition of 79 parts HMA, 20.7 parts TBCM, and 0.3 parts ethylene glycol dimethacrylate (EGDMA) gave a transparent, flexible film possessing a water content of 72.6%, a Young's modulus of 0.45 MPa, oxygen permeability of 28 barrers, and a tear strength of 28 N/m. In contrast, a copolymer composition of 40 parts HMA, 59.7 parts TBCM, and 0.3 parts EGDMA gave a hard, transparent film possessing a water content of 33% and a modulus of 504 MPa.

© 1993 John Wiley & Sons, Inc.

INTRODUCTION

Hydrogels are hydrophilic polymers that absorb water to an equilibrium value and are insoluble in water due to the presence of a three-dimensional network.¹ The hydrophilicity is due to the presence of hydrophilic groups, such as alcohols, carboxylic acids, amides, and sulfonic acids. The swollen equilibrated state results from a balance between the osmotic driving forces that cause the water to enter the hydrophilic polymer and the forces exerted by the polymer chains in resisting expansion.¹⁻⁴

Hydrogels, both the natural and synthetic, have given rise to a wide variety of materials for biomedical use in diagnostic and therapeutic devices for both short-term and long-term applications. These applications include such uses as catheters,^{5,6} hemodialysis membranes,⁷ degradable therapeutic systems,⁸ drug-delivery systems,⁹ and contact lenses.^{1,10,11}

The successful design of new polymeric materials for contact lens application requires an extensive knowledge of polymer chemistry, polymer properties, and the physiology of the eye.^{1,12} The properties that must be optimized in designing a new contact lens material are optical transparency, chemical and thermal stability, wettability to tears, mechanical properties, biological compatibility, and oxygen permeability.

There exist two basic methods for the development of hydrogels with high oxygen permeability. The first method involves the copolymerization of polydimethylsiloxane (PDMS) with hydrophilic monomers. Since PDMS possesses an extremely high permeability to oxygen, the incorporation of PDMS as a copolymer with hydrophilic monomers results in hydrogels possessing a high permeability to oxygen; however, the increase in concentration of PDMS also results in a reduction in water content, lens clarity, and surface wettability.¹³ The second method involves the design of high water content hydrogels (> 55%). The use of high water content hydrogels for contact lens application has been ex-

* To whom correspondence should be addressed.

tensively studied.^{14,15} The high water contact lens material increases the supply of oxygen to the cornea (the higher the water content, the higher the oxygen permeability of the hydrogel).¹⁶ This oxygen supply is sufficient to minimize the corneal edemic response associated with extended periods of contact lens wear.

The design of high water content materials involves two approaches: The first approach involves the polymerization of highly hydrophilic nonionic monomers such as *N*-vinyl pyrrolidinone (NVP) and acrylamide (AA) with hydrophobic monomers, such as cyclohexyl methacrylate (CHM) and methyl methacrylate (MMA). The second approach involves the copolymerization of moderately hydrophilic monomers, such as hydroxyethyl methacrylate (HEMA), with highly hydrophilic, ionic monomers such as methacrylic acid. The ionic functionality, in a buffered saline environment (pH 7.35–7.45), dramatically increases the water content of the resultant hydrogel. For example, a formulation consisting of 94% w/w HEMA copolymerized with 6% w/w methacrylic acid results in a hydrogel, following a buffered saline hydration, containing 70% water [a film of poly (HEMA) without methacrylic acid contains approximately 39% water].

There are two basic limitations of the high water content lens materials. The first is that most high water content lens materials exhibit poor mechanical properties.¹⁷ High water content materials characteristically possess a low modulus of elasticity and low tensile and tear strength, resulting in poor lens handling characteristics and lens durability. Attempts to improve the mechanical properties by the copolymerization of bulky, hydrophobic monomers generally results in a phase-separated, opaque lens material and a dramatic reduction in water content. The second limitation of high water content lens materials is their high protein affinity, particularly for hydrogels that contain an ionic functionality, such as a carboxylic acid.¹⁸ During wear, protein is absorbed that replaces some of the absorbed water in the polymer and resulting in a significant reduction in oxygen permeability.¹⁹ Therefore, the direction in high-water contact lens research has been to design high-water materials that do not contain ionic functionalities and provide suitable mechanical properties.

This study describes the development of a novel, nonionic, high water content hydrogel based on *N*-(2-hydroxyethyl) methacrylamide (HMA), 2-hydroxyethyl methacrylate (HEMA), and 4-*t*-butyl-2-hydroxycyclohexyl methacrylate (TBCM). Hydrogels prepared from HMA and HEMA with vary-

ing concentrations of TBCM have provided lenses with a wide range of water content that are transparent, oxygen permeable, and possess excellent mechanical properties.

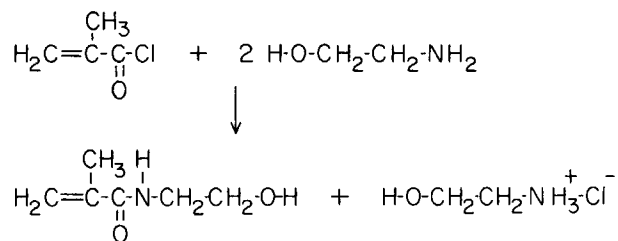
EXPERIMENTAL

Materials

Ethylene glycol was purchased from Aldrich Chemical Co. and used as received. Methacryloyl chloride and ethanolamine (both from Aldrich) were distilled prior to use. Benzoin methyl ether (BME), also from Aldrich, was crystallized from ligroin before use. Ethylene glycol dimethacrylate and HEMA were purchased from Sartomer and distilled under vacuum before use. The TBCM was prepared according to a procedure described in a previous publication.²⁰ All other solvents and reagents were used as received.

Synthesis of *N*-(2-hydroxyethyl) methacrylamide (HMA) (Scheme 1)

Methacryloyl chloride (104.5 g, 1.50 mol) was slowly added to a cooled solution (0°C) of ethanolamine (188.7 g, 3.09 mol) in 800 mL of freshly distilled THF. The addition required 2 h and the reaction temperature was not allowed to exceed 5°C. After the addition was complete, the reaction mixture was filtered cold through a Buechner funnel to remove the amine hydrochloride salt. The filtrate was then placed on a 10 × 40 cm column of activated alumina and eluted with ethyl acetate. The collected eluant was placed on a rotary evaporator and the ethyl acetate and THF were removed. The resultant crude HMA was then distilled using a Kuegelrohr distillation apparatus. Cuprous chloride (0.013 g, 0.13 mmol) and 2,5-diphenylbenzoquinone (0.013 g, 0.04 mmol) were used as polymerization inhibitors. The purified HMA (80 g, 62%) is 96% pure as shown by GC. ¹H-NMR (CDCl₃, TMS, δ, ppm): 1.95 (s, 3H,



Scheme 1 Synthetic route used in the preparation of HMA.

—CH₃), 3.3–3.8 (m, 4H, —CH₂—CH₂—), 4.5 (t, 1H, —C—O—H), 5.3 (s, 1H, =C—H), 5.7 (s, 1H, =C—H), 7.1 (s, 1H, N—H).

Techniques

Monomer purity was determined on a Hewlett-Packard HP5890A GC using a 6.1 m × 0.32 cm column of 10% SP-1000 80/100 Supelcoport. Monomer structure was confirmed by 60 MHz ¹H-NMR spectroscopy using a Varian EM 360 spectrometer. Films were cast between silanized glass plates using a 0.3 mm Teflon spacer. The glass silanization procedure consists of dipping the glass plates (8.3 × 10.2 cm) in a 20% v/v solution of trimethylchlorosilane in heptane followed by rinsing the glass plates in distilled water and air drying. The cure conditions were established through a thorough investigation of initiators, diluent concentration, and temperature to optimize vinyl conversion and percent water extractables. The optimum cure conditions consisted of 30 min of UV (2500 uW/cm²) at room temperature followed by 45 min of UV at 80°C using 0.2% BME as initiator and 15 parts ethylene glycol as diluent. The resultant films were extracted 2 h in distilled water and hydrated overnight at room temperature. The ethylene glycol is water soluble and is removed during the water-extraction process. The water content was determined using the following equation:

$$\% \text{ H}_2\text{O} = (\text{hydrated weight} - \text{dry weight} / \text{hydrated weight}) \times 100$$

The mechanical properties of films were determined on an Instron Model 4500 using ASTM methods 1708 and 1938. Glass transition temperatures were measured on a DuPont 942 thermal mechanical analyzer (20°C/min). Oxygen permeability (DK) was determined using the polarographic probe method.²¹

RESULTS AND DISCUSSION

The primary goal of this study was to develop a new nonionic, high-strength high water content hydrogel based on *N*-(2-hydroxyethyl) methacrylamide (HMA) suitable for extended wear contact lenses. The HMA, due to its highly hydrophilic amide linkage and terminal hydroxy group, we felt would provide a polymer capable of absorbing large quantities of water. The preparation of HMA and similar an-

alogs has been described in the literature; however, despite its structural similarity to 2-hydroxyethyl methacrylate (HEMA), HMA has not been described in the literature for use in contact lens materials and has only seen limited use for biomedical applications.^{22–25}

The physical and mechanical properties that we hoped to achieve in this study included a Young's modulus between 0.20 and 1.0 MPa, a tear strength greater than 25 N/m, water extractables below 10%, a DK greater than 20 barrers, and water contents between 55 and 80%. These physical and mechanical property objectives were chosen based on clinical experience with a variety of commercial and experimental hydrogel lens materials.

Scheme 1 outlines the synthetic procedure used to prepare HMA. This involved the low-temperature reaction of methacryloyl chloride with ethanol amine. The purification was completed by passing HMA through a column of activated alumina followed by distillation using a Kuegelrohr distillation apparatus. The purified HMA was 96% pure as shown by GC and the structure was confirmed by ¹H-NMR spectroscopy. It is important to note that the combined use of alumina and the Kuegelrohr distillation apparatus was essential to obtain consistently high yields of HMA. Without this combined purification scheme, the HMA prematurely polymerizes during the distillation step.

Films were cast of HMA between silanized glass plates with varying concentrations of ethylene glycol dimethacrylate as a cross-linker. The films were cured using 30 min of UV at room temperature followed by 45 min of UV at 80°C. The films were fully cured as determined by NIR spectroscopy. The films were extracted 2 h in distilled water at 80°C and hydrated overnight at room temperature. The percent water of the resultant clear films was 90%; however, the films were mechanically weak and difficult to handle without breakage. Because of the poor mechanical properties of this material, no further work was completed on this formulation.

The next phase of this work consisted of attempting to improve the mechanical properties of the HMA films while maintaining the high water content and film clarity. It was shown in a previous study that the use of the "hydrophilic-bulky" monomer 4-*t*-butyl-2-hydroxycyclohexyl methacrylate (TBCM) dramatically improved the strength of some hydrogel formulations.²⁰ For example, the copolymerization of TBCM in varying concentrations with NVP dramatically increased the modulus, tensile strength, and tear strength of the resultant TBCM/NVP copolymers, while maintaining film

clarity and a high water content. This result was attributed to an increase in the polymer backbone rigidity (due to the *t*-butylcyclohexyl group) and better compatibility with hydrophilic monomers (due to the secondary hydroxy group).

Films were then cast with HMA and varying concentrations of TBCM and a cross-linker ethylene glycol dimethacrylate (EGDMA). The TBCM concentration varied from 10 to 60 wt % and the EGDMA concentration varied from 0.3 to 0.9 wt %. All the films cast were transparent. Table I summarizes the mechanical and physical property results for the HMA/TBCM formulations. All the formulations were cast using 15 parts of ethylene glycol as diluent and 0.2% BME as the UV initiator. The ethylene glycol was added to the formulation to reduce the T_g of the resultant film below the cure temperature (to effect a complete cure), to control lens expansion, and to reduce the viscosity of the formulation. Near-infrared analysis of the films following the cure cycle showed the complete loss of

vinyl. Also included in Table I are the mechanical and physical properties of poly(HEMA). A wide range in mechanical and physical properties were observed for the HMA/TBCM/EGDMA films.

Figure 1 shows the dependence of modulus and percent water on TBCM concentration for the HMA/TBCM/EGDMA formulations. A significant increase in modulus and decrease in percent water occurred with increasing concentration of TBCM. In addition, an increase in tear strength and tensile strength occurred with increasing concentration of TBCM. Figure 2 shows the dependence of modulus on TBCM concentration with varying levels of EGDMA. An increase in EGDMA resulted in a significant increase in modulus. In addition, an increase in the EGDMA concentration resulted in an increase in the tear strength and decreases in water content and oxygen permeability. The 79/20.7/0.3 (HMA/TBCM/EGDMA) formulation resulted in a high water material (72.6%) having a tear strength of 28 N/m, a modulus of 0.45 MPa, water extractables of

Table I Mechanical and Physical Property Results for the HMA/TBCM/EGDMA-based Formulations

Formulation ^a (wt %)	Modulus (MPa)	Tensile (MPa)	Elongation (%)	Tear (N/m)	% H ₂ O	% Ext ^b	DK ^c
90/9.7/0.3	0.18 ± 0.01	0.08 ± 0.01	62 ± 9	8 ± 0.4	83.1 ± 1.0	28.0 ± 0.2	42 ± 2.1
90/9.4/0.6	0.32 ± 0.02	0.13 ± 0.01	55 ± 8	9 ± 0.4	79.0 ± 1.0	27.0 ± 0.2	40 ± 2.0
90/9.1/0.9	0.49 ± 0.02	0.25 ± 0.01	63 ± 9	13 ± 0.7	74.4 ± 0.9	19.9 ± 0.2	34 ± 1.7
85/14.7/0.3	0.23 ± 0.01	0.13 ± 0.01	86 ± 13	11 ± 0.6	79.0 ± 1.0	26.9 ± 0.2	39 ± 2.0
85/14.4/0.6	0.38 ± 0.02	0.23 ± 0.01	86 ± 13	11 ± 0.6	76.5 ± 1.0	27.3 ± 0.3	37 ± 1.9
80/19.7/0.3	0.26 ± 0.01	0.26 ± 0.01	158 ± 24	17 ± 0.9	77.6 ± 1.0	27.2 ± 0.1	36 ± 1.8
80/19.4/0.6	0.54 ± 0.02	0.24 ± 0.01	71 ± 11	25 ± 1.3	70.9 ± 0.9	25.6 ± 0.3	31 ± 1.6
79/20.7/0.3	0.45 ± 0.02	0.57 ± 0.03	183 ± 28	28 ± 1.2	72.6 ± 1.0	20.2 ± 0.3	28 ± 1.4
79/20.4/0.6	0.67 ± 0.03	0.44 ± 0.02	96 ± 15	28 ± 1.4	68.8 ± 0.8	18.9 ± 0.4	28 ± 1.4
79/20.1/0.9	0.75 ± 0.04	0.52 ± 0.03	95 ± 15	22 ± 1.1	67.5 ± 0.8	20.0 ± 0.2	27 ± 1.4
77/22.7/0.3	0.53 ± 0.03	0.59 ± 0.03	167 ± 24	27 ± 1.4	71.3 ± 1.0	18.6 ± 0.1	26 ± 1.3
77/22.4/0.6	0.74 ± 0.04	0.70 ± 0.04	133 ± 20	32 ± 1.6	67.9 ± 0.8	18.6 ± 0.1	26 ± 1.3
77/22.1/0.9	1.0 ± 0.05	0.60 ± 0.03	85 ± 13	27 ± 1.4	66.0 ± 0.8	19.2 ± 0.1	24 ± 1.2
75/24.7/0.3	0.63 ± 0.03	0.91 ± 0.05	188 ± 28	36 ± 1.8	72.4 ± 1.0	18.0 ± 0.2	30 ± 1.5
75/24.4/0.6	0.92 ± 0.05	0.72 ± 0.04	141 ± 21	44 ± 2.2	68.9 ± 0.9	24.4 ± 0.2	28 ± 1.4
70/29.7/0.3	2.3 ± 0.11	1.14 ± 0.05	184 ± 28	70 ± 3.5	65.9 ± 1.0	16.8 ± 0.1	28 ± 1.4
60/39.7/0.3	51.7 ± 2.6	3.0 ± 0.15	122 ± 18	570 ± 28	51.5 ± 0.7	22.8 ± 0.1	13 ± 0.7
50/49.7/0.3	194.0 ± 9.7	5.8 ± 0.30	74 ± 11	2030 ± 101	38.5 ± 0.3	22.7 ± 0.3	5 ± 0.3
40/59.7/0.3	504.0 ± 25.2	15.9 ± 0.80	6 ± 0.9	—	33.0 ± 0.3	18.9 ± 0.4	3 ± 0.3
HEMA	0.75 ± 0.04	0.56 ± 0.03	197 ± 30	58 ± 2.9	38.0 ± 0.3	17.0 ± 0.1	10 ± 0.5

^a All formulations consist of 0.2% BME as initiator.

^b 15 parts of ethylene glycol was added as diluent and is removed during the water extraction process.

^c DK in units of [cm³ O₂ (STP) cm]/(s cm² mmHg) × 10⁻¹¹.

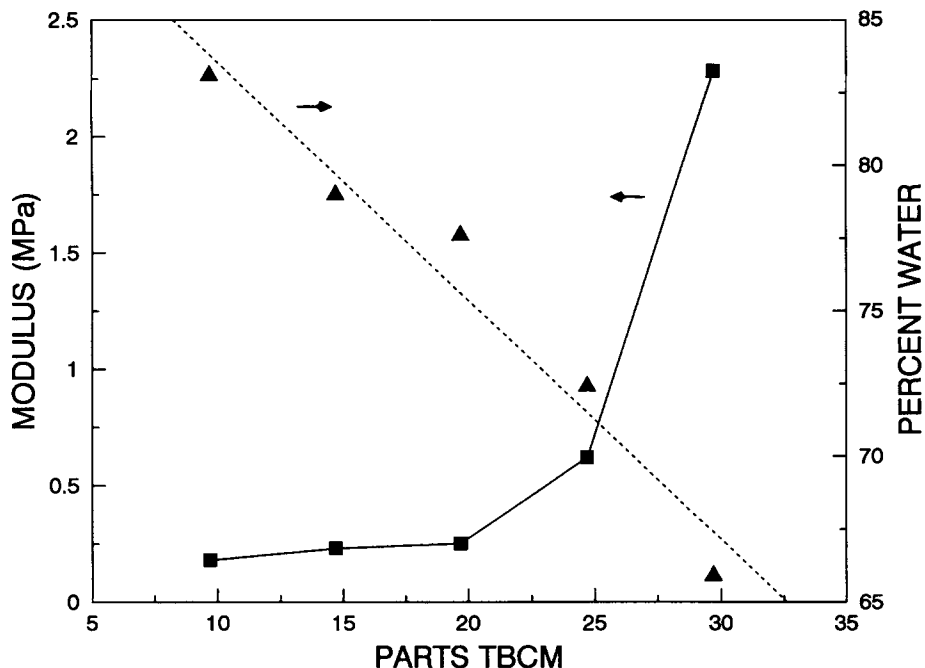


Figure 1 Dependence of parts TBCM vs. (■) modulus and (Δ) percent water for formulations based on HMA and TBCM (all formulations consist of 0.2% BME as initiator and 0.3% EGDMA as cross-linker).

5.2% (excluding the diluent), and a DK of 28. In contrast, the 40/59.7/0.3 (HMA/TBCM/EGDMA) formulation possessed a modulus of 504 MPa (a modulus approximately one-third that of

PMMA) and still absorbed 33% water. Figure 3 shows the relationship between water content on oxygen permeability (DK) for the HMA/TBCM/EGDMA formulations. The oxygen permeability for

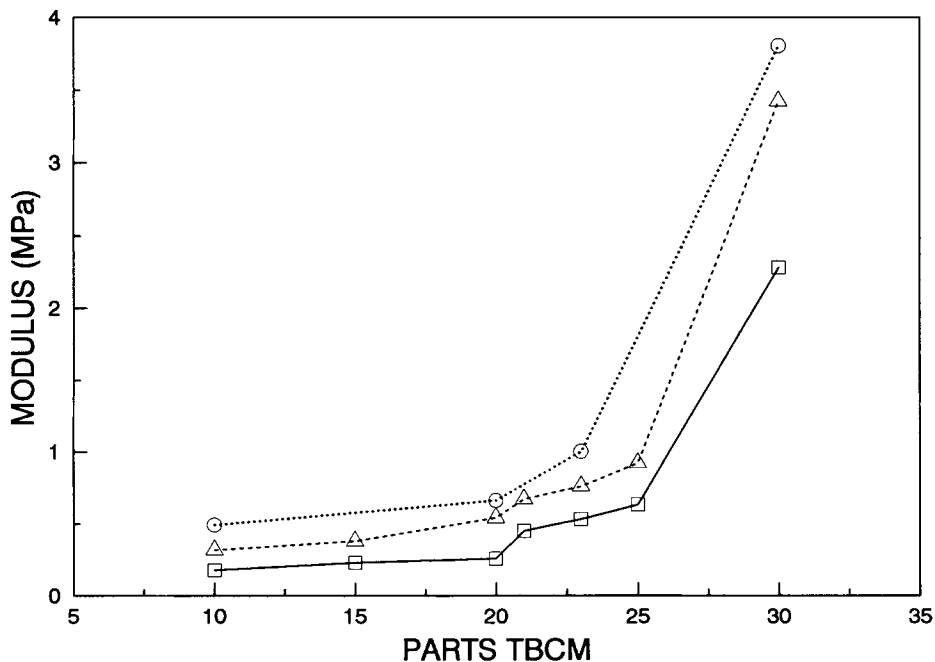


Figure 2 Dependence of parts TBCM vs. modulus (MPa) with (□) 0.3 parts, (Δ) 0.6 parts, and (○) 0.9 parts EGDMA for formulations based on HMA, TBCM, and EGDMA.

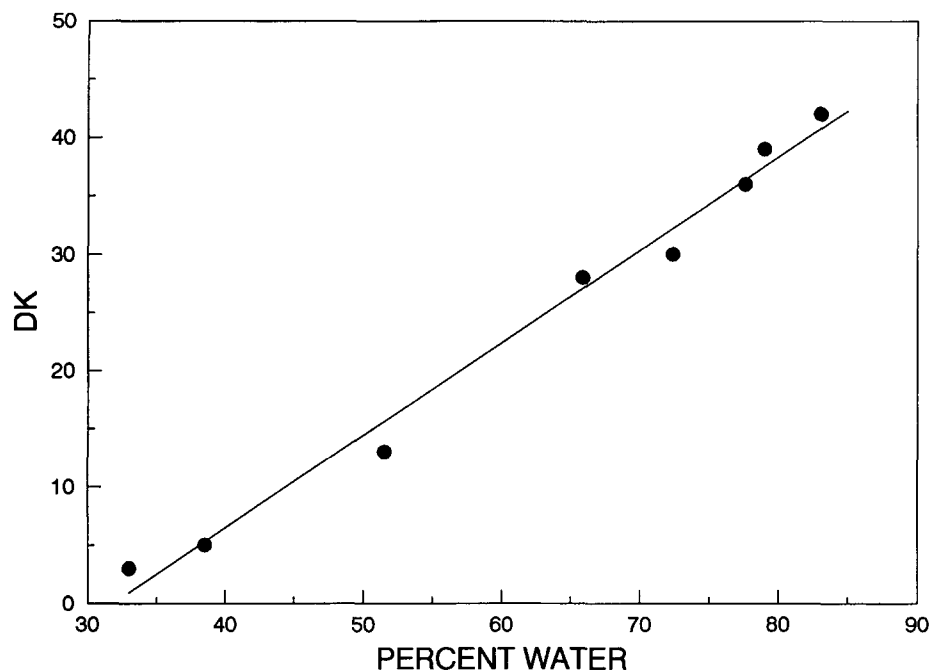


Figure 3 Dependence of oxygen permeability (DK) vs. percent water for hydrogels based on HMA and TBCM with 0.3% EGDMA [DK in units of $[\text{cm}^3 \text{O}_2(\text{STP})\text{cm}]/(\text{s cm}^2 \text{mmHg}) \times 10^{-11}$].

the 79/20.7/0.3 (HMA/TBCM/EGDMA) formulation represents a threefold increase in oxygen permeability compared to poly(HEMA). This in-

crease in permeability will result in significantly reduced corneal swelling with wear time.

Table I lists a number of HMA/TBCM copoly-

Table II Mechanical and Physical Property Results for the HMA/HEMA/TBCM-based Formulations

Formulation ^a (wt %)	Modulus (MPa)	Tensile (MPa)	Elongation (%)	Tear (N/m)	% H ₂ O	% Ext ^b	DK ^c
90/0/10	0.18 ± 0.01	0.08 ± 0.01	62 ± 9	8 ± 0.4	83.1 ± 0.8	28.0 ± 0.6	42 ± 2.1
70/20/10	0.31 ± 0.02	0.14 ± 0.01	59 ± 9	12 ± 0.6	73.5 ± 0.7	20.5 ± 0.4	34 ± 1.7
60/30/10	0.55 ± 0.03	0.23 ± 0.01	51 ± 8	15 ± 0.8	67.8 ± 0.7	25.0 ± 0.5	28 ± 1.4
45/45/10	0.53 ± 0.03	0.43 ± 0.02	133 ± 20	16 ± 0.8	63.9 ± 0.6	19.2 ± 0.4	24 ± 1.2
25/65/10	0.70 ± 0.04	0.67 ± 0.03	138 ± 20	42 ± 2.0	49.5 ± 0.5	16.9 ± 0.4	13 ± 0.7
85/0/15	0.23 ± 0.01	0.13 ± 0.01	86 ± 13	11 ± 0.6	79.0 ± 0.8	26.9 ± 0.6	39 ± 2.0
70/15/15	0.33 ± 0.02	0.29 ± 0.01	132 ± 20	17 ± 0.6	73.1 ± 0.7	21.4 ± 0.4	34 ± 1.7
65/20/15	0.31 ± 0.02	0.21 ± 0.01	101 ± 15	23 ± 1.0	71.5 ± 0.7	21.3 ± 0.4	32 ± 1.9
60/25/15	0.32 ± 0.02	0.38 ± 0.02	183 ± 27	31 ± 2.0	69.7 ± 0.7	21.5 ± 0.4	31 ± 1.9
25/60/15	0.85 ± 0.04	0.79 ± 0.04	157 ± 24	85 ± 4.3	45.9 ± 0.5	17.4 ± 0.4	11 ± 0.6
80/0/20	0.26 ± 0.01	0.26 ± 0.01	158 ± 24	17 ± 0.8	77.6 ± 0.8	27.2 ± 0.6	36 ± 1.8
50/30/20	0.56 ± 0.03	0.77 ± 0.04	234 ± 35	44 ± 2.0	58.7 ± 0.6	19.2 ± 0.4	20 ± 1.0
40/40/20	0.62 ± 0.03	0.61 ± 0.03	208 ± 31	64 ± 3.2	57.0 ± 0.6	16.9 ± 0.4	19 ± 1.0
70/0/30	0.28 ± 0.11	1.14 ± 0.06	184 ± 27	70 ± 3.5	65.9 ± 0.7	16.8 ± 0.4	28 ± 1.4
60/10/30	5.43 ± 0.27	1.30 ± 0.08	131 ± 20	10.4 ± 0.5	60.7 ± 0.6	20.1 ± 0.4	22 ± 1.1
25/45/30	106.0 ± 5.30	6.0 ± 0.30	81 ± 13	1820 ± 95	36.0 ± 0.4	18.3 ± 0.4	5 ± 0.3
HEMA	0.75 ± 0.04	0.56 ± 0.03	197 ± 30	58 ± 2.9	38.0 ± 0.3	17.0 ± 0.1	10 ± 0.5

^a All formulations consist of 0.2% BME as initiator and 0.3% EGDMA as cross-linker.

^b 15 parts of ethylene glycol was added as diluent and is removed during the water extraction process.

^c DK in units of $[\text{cm}^3 \text{O}_2(\text{STP})\text{cm}]/(\text{s cm}^2 \text{mmHg}) \times 10^{-11}$.

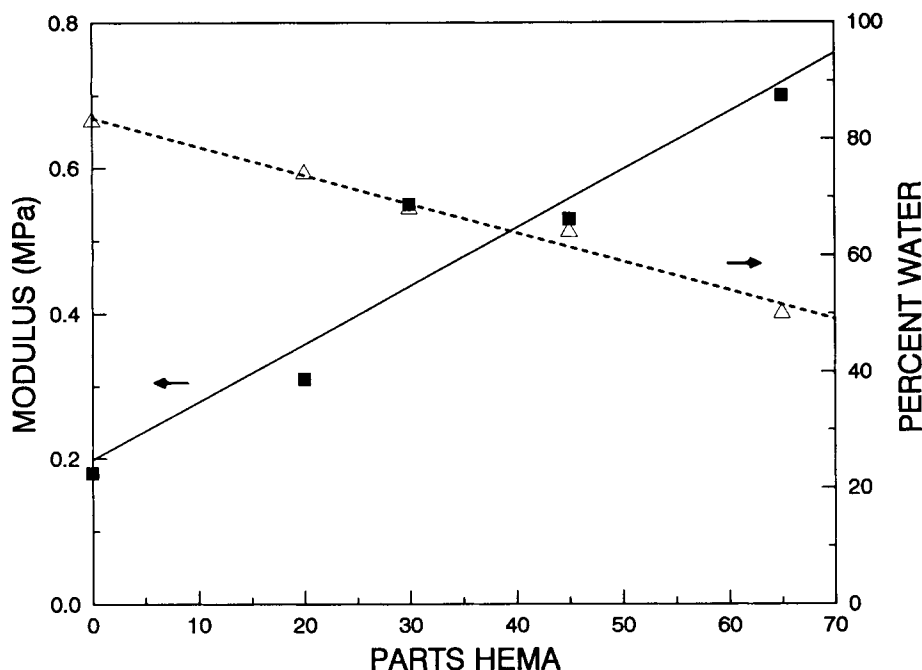


Figure 4 Dependence of parts HEMA vs. (■) modulus and (△) percent water for formulations based on HMA, HEMA, and TBCM (all formulations consist of 0.2% BME as initiator and 0.3% EGDMA as cross-linker).

mer compositions that show promise for contact lens application. Acceptable modulus, tear strength, water extractables, and oxygen permeability values were obtained for the HMA/TBCM copolymers when using a 20–25 wt % concentration of TBCM. We were unable, however, to achieve acceptable modulus values in the 55–65% water content range.

The final phase of this work consisted of attempting to develop formulations based on HMA/TBCM that have the desired mechanical and physical properties in the 55–65% water content range. It has been shown in previous work that the copolymerization of moderately hydrophilic monomers, such as HEMA, in increasing concentrations with highly hydrophilic monomers, such as *N*-vinyl pyrrolidinone (NVP), dramatically lowered the water content and improved the mechanical properties of the NVP/HEMA hydrogel.¹⁹ A similar approach was pursued in this study.

Films were cast between silanized glass plates from HMA and TBCM with varying concentrations of HEMA. In this work, the HEMA concentration varied from 20 to 65 wt % (replacing HMA in increasing concentrations). The TBCM concentration varied from 10 to 30 parts and the EGDMA concentration was kept constant. Table II summarizes the mechanical and physical property results for the HMA/HEMA/TBCM formulations. All the films

cast were transparent. All the formulations were again cast using 15 parts of ethylene glycol as diluent and 0.2% BME as the UV initiator. Figure 4 shows the dependence of parts HEMA vs. percent water and modulus for the HMA/HEMA/TBCM formulations. A decrease in water content with a corresponding increase in tear strength, tensile strength, and modulus were observed for formulations with an increasing concentration of HEMA. Acceptable modulus values were obtained in the 50–65% water content range. For example, the 40/40/20 (HMA/HEMA/TBCM) formulation possessed a water content of 57%, a modulus of 0.62 MPa, and a tear strength of 64 N/m. In contrast, the 60/39.7/0.3 (HMA/TBCM/EGDMA) formulation, without HEMA, had a comparable water content (52%), yet possessed a modulus of 51.7 MPa.

CONCLUSION

In conclusion, new nonionic high water content lens materials based on formulations consisting of *N*-(2-hydroxyethyl)-methacrylamide, 2-hydroxyethyl methacrylate and 4-*t*-butyl-2-hydroxycyclohexyl methacrylate have been successfully prepared. The candidate formulations possessed high water content, high oxygen permeability, and excellent mechanical properties.

REFERENCES

1. V. Kudella, in *Encyclopedia of Polymer Science and Engineering*, J. I. Kroschwitz, Ed., Wiley-Interscience, New York, 1987, Vol. 7, p. 783.
2. J. D. Andrade, Ed., *Hydrogels for Medical and Related Applications*, ACS Symposium Series 31, American Chemical Society, Washington, DC, 1976.
3. J. M. Anderson, Ed., *Biomaterials 1984*, Transactions, Second World Congress of Biomaterials, 10th Annual Meeting, Society of Biomaterials, Washington, DC, 1984, Vol. 7, p. 20.
4. B. Ratner, in *Comprehensive Polymer Science*, S. L. Aggarwal, Ed., Pergamon Press, New York, 1988, Vol. 7, p. 222.
5. A. L. Kaganov, J. Stamberg, and P. Synek, *J. Biomed. Mater. Res.*, **10**, 1 (1976).
6. G. S. Margules, C. M. Hunter, and D. C. MacGregor, *Med. Biol. Eng. Comput.*, **21**, 1 (1983).
7. J. Kopecek, in *Macromolecules*, H. Benoit and P. Rempt, Eds., Pergamon Press, New York, 1982, p. 305.
8. R. Duncan, J. Kopecek, P. Rejmanova, and J. B. Lloyd, *Biochim. Biophys. Acta*, **755**, 518 (1983).
9. J. Drobic, *The Use of Polymers in Medicine*, The Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, 1977, Vol. B-1.
10. N. A. Peppas and W. M. Yang, *Contact Lens*, **7**, 302 (1981).
11. P. L. Keogh, *Biomat. Med. Dev. Art. Org.*, **7**, 307 (1979).
12. B. Tighe, *Br. Polym. J.*, **18**, 8 (1986).
13. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, 3rd ed., Wiley-Interscience, New York, 1989, p. VI 435.
14. M. J. Refojo, in *Encyclopedia of Polymer Science and Technology*, Suppl. 1, N. M. Bikales, Ed., Wiley-Interscience, New York, 1976, pp. 195-205.
15. B. Tighe and D. Pedley, *Proceed. Int. Macromol. Symp. Int. Union Pure and Appl. Chem.*, **27**, 24 (1980).
16. B. Holden, G. Mertz, and J. McNally, *Invest. Ophthalmol. Vis. Sci.*, **24**, 218 (1983).
17. S. Hosaka, A. Yamada, H. Tazawa, T. Momose, H. Magatani, and A. Nakajima, *J. Biomed. Mater. Res.*, **14**, 557 (1980).
18. L. Minarik and J. Rapp, *C.L.O.A.*, **15**, 185 (1989).
19. J. Künzler and G. Friends, Bausch and Lomb Inc., unpublished results.
20. G. Friends and J. Künzler, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Mat. Sci. Eng.*, **62**, 809 (1990).
21. I. Fatt, J. E. Rasson, and J. B. Melpolder, *Int. Contact Lens Clin.*, **14**, 38 (1987).
22. G. D. Jones, U.S. Pat. 2,593,888 (1952); *Chem. Abstr.*, **46**, 8553g (1952).
23. J. Brown, P. Goddard, and K. Petrak, *J. Polym. Sci. Polym. Lett. Ed.*, **27**, 515 (1989).
24. J. Vacik, L. Shataeva, G. Samsonov, J. Kalal, and J. Kopecek, *Collect. Czech. Chem. Commun.*, **44**, 1931 (1979).
25. Y. Murashige and J. Fujimoto, Jpn. Pat. 61-068454 (1986); *Chem. Abstr.*, **105**, 134491f (1986).

Received February 18, 1992

Accepted January 14, 1993