The Role of Bulky Polysiloxanylalkyl Methacrylates in Polyurethane–Polysiloxane Hydrogels

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SYNOPSIS

Silicone hydrogels based on polyurethane–polysiloxane prepolymers and hydrophilic monomers such as *N,N*-dimethylacrylamide, although possessing high oxygen permeability and satisfactory tear strength, are too stiff to be targeted for applications such as contact lenses. However, with the inclusion of bulky polysiloxanylalkyl methacrylates, such as methacryloxypropyl tris(trimethylsiloxy)silane (TRIS), to replace part of the polyurethane prepolymer, the hydrogels obtained not only maintained high oxygen permeability, but also had a lower modulus and improved tear strength. These changes in properties are all favorable for applications such as oxygen-permeable hydrogel lenses. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Hydrogels are water-containing polymer networks derived from various kinds of hydrophilic monomers and often modified with hydrophobic monomers. The water content, modulus, and tear strength of hydrogels depend on the nature of the monomers and crosslinking density.[1] Hydrogels have been used in a variety of applications, especially as contact lenses. Currently marketed contact lens materials are derived almost exclusively from 2-hydroxyethyl methacrylate (HEMA), glycerol methacrylate, or *N*-vinylpyrrolidone.[1] Hydrogels which are currently used as contact lens have water contents ranging from 38 to 75%. The oxygen permeability of these hydrogel materials, which depends exclusively on water content, falls in the range of 8–40 in Barrer units (1 Barrer = 1 Dk = 1×10^{-11} cm^2 mL O_2/s mL mmHg). The tensile moduli of these hydrogels are in the range of 20–140 g/mm^2, and tear strengths are in the range of 1–5 g/mm.

Existing hydrogel lenses are, in general, comfortable to wear and suitable for daily wear. Because of insufficient oxygen transport, they caused corneal swelling in overnight wear due to hypoxia.[2] However, this corneal swelling recovers to normal during the daytime. It was suggested that the oxygen transmissibility of a lens, defined as Dk/L (oxygen permeability divided by lens thickness), should be at least 87×10^{-9} cm mL O_2/s mL mmHg for a human corneal overnight swelling to be equivalent to a no-lens situation.[3] Attempts to increase oxygen transport, by either using material with higher water or thinner hydrogel lens, did not generate satisfactory results due to other complications.[1]

Polysiloxane-based elastomers, or silicone rubber, are known to be highly oxygen-permeable. Oxygen permeability as high as 600 Barrers was claimed for polydimethylsiloxane.[4] Because of high oxygen permeability, silicone elastomers have long been considered excellent candidates for contact lens materials.[5] In addition to silicone elastomers, monomers and prepolymers containing siloxane groups have been prepared and used in combination with other monomers to give oxygen-permeable polymeric materials. These monomers and prepolymers were claimed to be useful for contact lens applications. For example, bulky polysiloxanylalkyl acrylic esters were incorporated into compositions to fabricate hard lenses in the early 1970s.[6] Since then, this class of silicone–acrylate monomers[7–9] and their styrene,[10] itaconate,[11] and dimer[11,12] analogs, particularly

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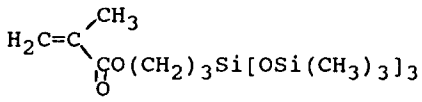
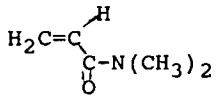
methacryloxypropyl tris(trimethylsiloxy)silane (TRIS, **1**),



have been used extensively in the development of rigid gas-permeable lens materials.

TRIS or its analogs has seldom been mentioned in patents[8,13] for its use as components of soft hydrogel lenses with improved oxygen permeability. In those cases, TRIS or its methacrylamide analog were used in combination with hydrophilic monomers such as *N,N*-dimethyl acrylamide (DMA, **2**),



to form hydrogels with good oxygen permeability.

In our earlier work on hydrogel materials based on a poly(propylene glycol)-based polyurethane prepolymer and a hydrophilic monomer, TRIS was incorporated into these compositions to obtain hydrogels with improved oxygen permeability.[14,15] In yet another approach to obtain high oxygen permeability for hydrogels, polyurethane prepolymers based on polysiloxanes having different arrangements of hard and soft segments were prepared.[16] These prepolymers were formulated with DMA to give hydrogels with good oxygen permeability.[17] In this article, the role of bulky polysiloxanylalkyl methacrylates such as TRIS in silicone hydrogels based on methacrylate-capped polyurethane–polysiloxane prepolymers is described.

EXPERIMENTAL

Monomers and Prepolymers

TRIS (over 98.5% purity, containing less than 0.02% of the dimer) was obtained from Silar Inc. and used as received. *N,N,*-Dimethylacrylamide and *n*-hexanol, both from Aldrich Chemical Co., and Darocur-1173 from EM Science were used as received. The preparations of the prepolymers with urethane linkages are described elsewhere.[16]

Hydrogel Synthesis

A polydimethylsiloxane-based polyurethane prepolymer, TRIS, and a hydrophilic monomer, in a weight ratio chosen to total 100 parts, were mixed with 40 parts of *n*-hexanol and 0.2 parts of Darocur-1173. The monomer mix was introduced between two glass plates (10 × 8 cm) and cured under a long-wave UV lamp (from UVP) for 2 h. The film thickness was controlled by a Teflon gasket material which gave a fairly consistent thickness of 0.25 mm. The films were extracted with ethanol for 16 h, dried in a vacuum oven at 70°C for 16 h, boiled with distilled water for 4 h, and swollen to equilibrium in phosphate-buffered saline (with pH 7.30) before characterization.

Characterization of Hydrogel Films

The water contents of hydrogels and the amounts of extractable cured films in ethanol were measured gravimetrically. Mechanical testing was conducted in a phosphate-buffered saline on an Instron instrument, according to the modified ASTM D-1708 (tensile) and D-1938 (tear) procedures and were reported in g/mm^2 (1 MPa = 102 g/mm^2) for tensile strength and modulus and in g/mm (1 kN/m = 1020 g/mm) for tear strength. The oxygen permeabilities were measured by the one chamber method[18] with consideration of edge effect and probe configuration and were reported in units of Barrer (1 Barrer = 10^{-11} cm^2 mL O_2/s mL mmHg).

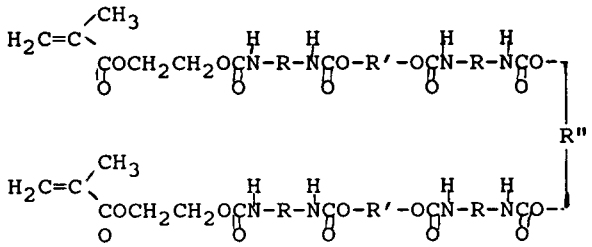
RESULTS AND DISCUSSION

Silicone Hydrogels Based on Polyurethane–Polysiloxane Prepolymers and DMA

For contact lens applications of hydrogels, all key properties must meet certain requirements. The main interest in silicone hydrogels is to use them as highly oxygen permeable lens materials for extended eye wear. Thus, for this particular application, the silicone hydrogels of interest must have high oxygen transmissibility (e.g., > 87 × 10^{-9} cm mL O_2/s mL mmHg), a modulus between 20 and 150 g/mm^2, and a tear strength above 3 g/mm.

Silicone hydrogels based on polyurethane–polysiloxane Prepolymers and DNA were reported previously.[17] These hydrogels were intended for applications in the biomedical area. Polyurethane–polysiloxane prepolymers of structures shown as **3** or **4** were prepared and used in making these hydrogels. Prepolymers with structure **3** are those having well-

defined hard–soft–hard blocks like traditional polyurethane elastomers, except being end-capped with HEMA. They are derived from sophorone diisocyanate (IPDI), neopentyl glycol (NPG), diethylene glycol (DEG), and hydroxybutyl-terminated polydimethylsiloxanes (HB-PDMS). Reversing R′ and R″ in structure **3** gives a prepolymer with a soft–hard–soft segment. A prepolymer of structure **4** does not have a well-defined hard segment, in which IPDI served as the linkage between HB-PDMS and HEMA, and it was prepared only for comparison:



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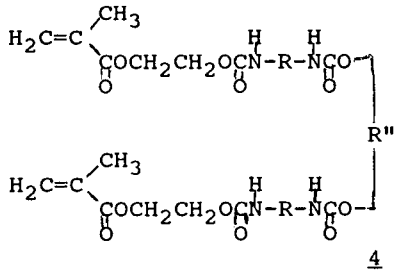

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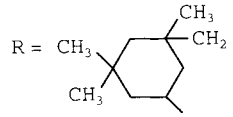
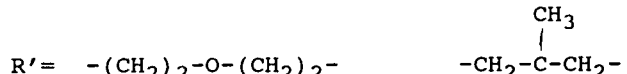


(IPDI)



(DEG) (NPG)

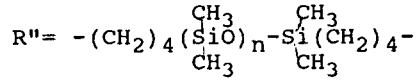


Table I lists prepolymers of these structures which were used in formulation studies to give hydrogels. For simplicity, abbreviations for prepolymers were given according to the components used in preparing them. For example, IDS3H, IDS4.5H, INS3H, and INS4.5H represent prepolymers derived from IPDI, DEG (or NPG), and HB-PDMS of molecular weight 3000 and 4500 and end-capped with HEMA and having structure **3**. IDS4.5HA has the same structure, but has $\frac{1}{4}$ of the HEMA end-capping replaced with allyl alcohol. IS1.5NH represents a prepolymer with a soft–hard–soft segment, using HB-PDMS of molecular weight 1500 as the soft segment. IS3H is a prepolymer without a well-defined hard segment and has structure **4**.

Figure 1 shows the oxygen permeability–water relationship of silicone hydrogels based on polyurethane prepolymer IDS3H and DMA. Basically, the oxygen permeability depends on the siloxane content: It decreases with increasing water content from around 300 and bottoms at 40–50 when the water content reaches 60–65%. Because of this, it is not worthwhile to prepare a silicone hydrogel with a water content over 60% if oxygen permeability is the major concern. On the other hand, close examinations of tear strength and modulus for hydrogels derived from INS3H/DMA and IDS3H/DMA and having a water content less than 60%, as shown on Figure 2, revealed that either tear strength is acceptable while the modulus is unacceptable (i.e., over 150 g/mm) or vice versa. Table II gives the modulus and tear properties of hydrogels derived from the prepolymer/DMA at a 70/30 weight ratio, with the prepolymer of the three different classes. A comparison of these properties suggested that, even though these polyurethane-based hydrogels have excellent mechanical properties, it is impossible to maintain both modulus and tear strength in an acceptable range at the same time if the targeted application is contact lenses. The question is how to lower modulus and improve tear strength of a polyurethane–polysiloxane hydrogel while maintaining high oxygen permeability. It is known that the modulus can be lowered by reducing the crosslinking density, such as reducing the concentration of the prepolymer used, using more DMA or adding other monomers to the formulation. However, this would lower the oxygen permeability due to the change in the siloxane concentration, and it would lower the tear strength if the water content of the hydrogel increases as more DMA is used.

The Effect of TRIS on Properties of Polyurethane–Polysiloxane Hydrogels

Because polysiloxanylalkyl methacrylates such as TRIS are known to give hard lens material with high oxygen permeability, it was worthwhile to determine if TRIS can help maintain the high oxygen

Table I Polyurethane–Polysiloxane Prepolymers Used in This Study

	Polyurethane Components		
Prepolymer	Structure	Hard Segment	Soft Segment
DEG series			
IDS3H	Hard–soft–hard	IPDI, DEG	HB-PDMS-3000
IDS4.5H	Hard–soft–hard	IPDI, DEG	HB-PDMS-4500
IDS4.5HA[a]	Hard–soft–hard	IPDI, DEG	HB-PDMS-4500
NPG series			
INS3H	Hard–soft–hard	IPDI, NPG	HB-PDMS-3000
INS4.5H	Hard–soft–hard	IPDI, NPG	HB-PDMS-4500
IS1.5NH	Soft–hard–soft	IPDI, NPG	HB-PDMS-1500
IS3H	Soft	IPDI	HB-PDMS-3000

[a] One-quarter of the end-capping is the allyl group.

permeability of silicone hydrogels based on polyurethane–polysiloxane prepolymer and DMA, while lowering the modulus and improving the tear strength when part of prepolymer in the prepolymer/DMA formulation is replaced by TRIS.

To evaluate the effects of TRIS, hydrogel films of chosen formulations were prepared by, first, UV-curing of chosen formulations, followed by extracting cured films with a solvent (ethanol), and then equilibrating them with buffered saline. For convenience, 40 parts of *n*-hexanol was used as solvent in the film preparation.

In the following, the effect of TRIS on key properties of polyurethane–polysiloxane hydrogels is discussed. Hydrogels based on IS3H were included in this study.

Oxygen Permeability

When DMA at 30 wt % of the monomer composition was used, all hydrogels have a water content of 25% (within experimental error). Figure 3 shows the effect of TRIS on oxygen permeability for hydrogels derived from DEG-derived prepolymers and 30 parts of DMA. (The combined amount of prepolymer and TRIS is 70%). Figure 4 shows the same relationship for those silicone hydrogels based on NPG-derived polyurethane prepolymers. It was found that oxygen permeabilities of hydrogels derived from the same prepolymer, within experimental error, were constant irrespective of the amount of TRIS used to replace the prepolymer in the formulation. In addition, the oxygen permeabilities of all hydrogels are about the same (80–120 in Barrer units), indicating that the oxygen permeability of silicone hydrogels depends only on the Si content regardless of whether it comes from a linear polysiloxane in polyurethane prepolymers with different hard- and soft-segment structures or a bulky polysiloxane in a monomer. This can be further explained by the similar Si content in prepolymers and TRIS as shown below:

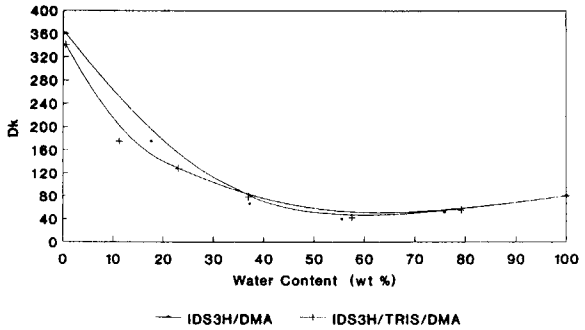


Figure 1 The relationship between oxygen permeability and water content in hydrogels derived from IDS3H, TRIS, and DMA.

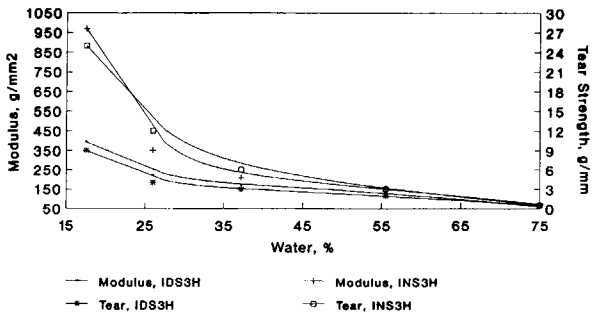


Figure 2 The relationship among modulus, tear strength, and water contents for hydrogels based on IDS3H/DMA and INS3H/DMA.

Monomer/Prepolymer	% Si
TRIS	26.5
IDS3H	24.8
IDS4.5H	27.3
IDS4.5HA	27.3
IS3H	29.5
IS1NH	23.4
INS3H	24.7
INS4.5H	27.2

Any minor difference in Si content in the prepolymer was further diluted by the water (25%) in silicone hydrogels. All polyurethane–polysiloxane hydrogels of this series have about 12–15% Si content. The hydrogels derived from IS3H have consistently higher oxygen permeability, possibly due to the increased flexibility of the prepolymer (no strong hard segments) as well as increased silicon content in the prepolymer. Figure 1, in addition to showing the relationship between oxygen permeability and water for hydrogels based on IDS3H/DMA, also illustrates the same relationship for hydrogels derived from IDS3H and DMA, with half of IDS3H replaced by TRIS. The equivalency of oxygen permeability for hydrogels with and without TRIS was observed. The oxygen permeability at a water content of 25% for these hydrogels is outstanding compared to those of traditional, nonsilicone hydrogels.

Table II Mechanical Properties of Cured Polyurethane Prepolymers and Hydrogels Derived from These Prepolymers and DMA at a 70 : 30 Weight Ratio

Prepolymer	Tensile Modulus (g/mm^2)	Tear Strength (g/mm)
DEG series		
IDS3H	220	4
IDS4.5H	180	3
IDS4.5HA	150	3
NPG series		
INS3H	350	9
INS4.5H	250	6
IS1NH	700	9
No clear hard segment		
IS3H	250	3

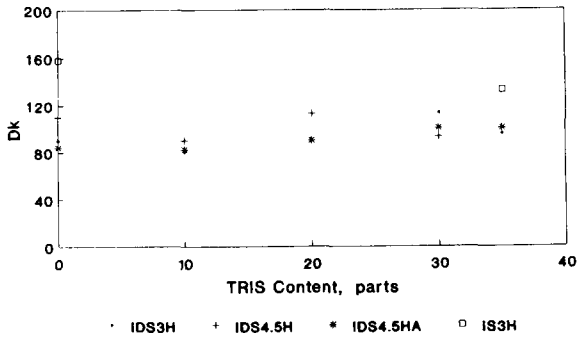


Figure 3 The relationship between oxygen permeability and TRIS in hydrogels (DEG series).

Mechanical Properties

Figure 5 shows the relationship between tensile modulus and wt % of TRIS used to replace the DEG-derived prepolymer in hydrogels derived from a prepolymer/DMA, with DMA at 30%, while the combined amount of the prepolymer and TRIS was at 70%.

Figure 6 shows the same relationship for the comparable hydrogels based on NPG-derived prepolymers. It was observed that, in all hydrogels, the modulus decreased as the amount of TRIS was increased. For example, without TRIS, the IDS3H/DMA-based hydrogel has a modulus of 220 g/mm2. But when TRIS was used to replace 10 parts of IDS3H, the modulus dropped to 170 and to around 100 g/mm2 when about half of IDS3H was replaced. Hydrogels based on other prepolymers, irrespective of their structure, showed roughly the same % of drop in modulus as TRIS was used to replace part of the prepolymer in a formulation. This is somewhat unexpected from the fact that TRIS is widely used in hard lenses. The reason for this phenomenon is that the overall crosslinking density and hard-segment fractions are reduced as the amount of TRIS is increased in the hydrogels.

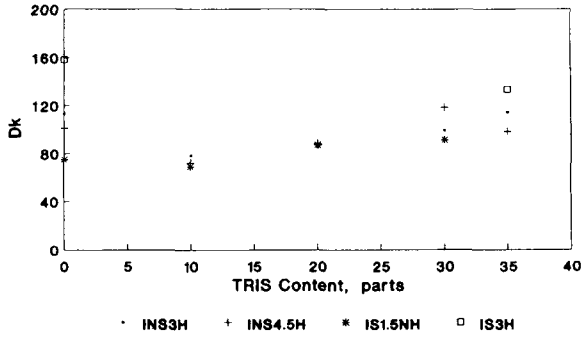


Figure 4 The relationship between oxygen permeability and TRIS in hydrogels (NPG series).

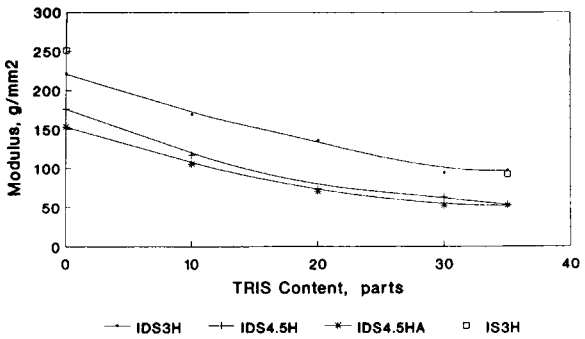


Figure 5 The relationship between tensile modulus and TRIS in hydrogels (DEG series).

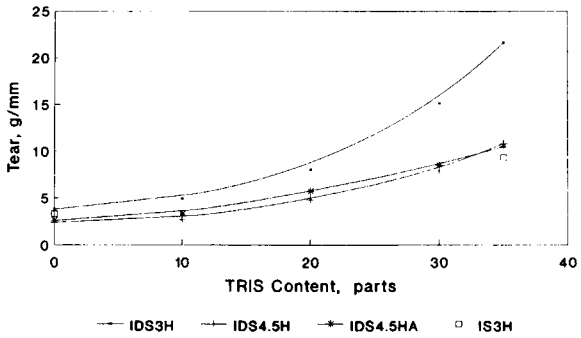


Figure 7 The relationship between tear strength and TRIS in hydrogels (DEG series).

Figure 7 gives the relationship between the tear strength of a polyurethane–polysiloxane hydrogel and the amount of TRIS used to replace a DEG-derived polyurethane prepolymer in a formulation containing 30% DMA. Figure 8 gives the same relationship for hydrogels based on NPG-derived polyurethane prepolymer. It is interesting to note that the tear strength increased with the amount of TRIS used to replace a prepolymer. For example, for hydrogels derived from IDS3H/DMA, the tear strength increased from 4 g/mm to over 15 g/mm when half of the prepolymer was replaced by TRIS. The same rate increases in tear strength in hydrogels based on other polyurethane prepolymers is also true. This means the tear strength consistently increases with reducing crosslinking density, which is true for most hydrogels. It should be noted here that silicone hydrogels derived from a polyurethane prepolymer with a weaker hard-segment structure (such as DEG-based prepolymer) usually gave poorer tear strength as compared to those derived from prepolymers with a stronger hard segment (such as NPG-based prepolymer). However, their tear strengths can be improved by using TRIS to replace part of the prepolymer used in the formulation. The anti-parallel relationship of modulus and tear strength with crosslinking density for this class of hydrogels is further demonstrated in Figure 9, which gives the modulus–tear strength relationship with TRIS in hydrogels based on IDS3H/TRIS/DMA.

One extra benefit of replacing part of the prepolymer with TRIS is that the % elongation of hydrogel films increased dramatically as the modulus decreases at the same time, which make these hydrogel materials more durable toward stretching.

The relationships among oxygen permeability, modulus, tear strength, and bulky polysiloxanylalkyl methacrylates, such as TRIS, in silicone hydrogels derived from polyurethane–polysiloxane prepolymers and hydrophilic monomer indicate that a bulky polysiloxanylalkyl methacrylate such as TRIS is an excellent monomer to employ in the quest for silicone hydrogels for contact lenses. This class of monomers is the only kind of monomer identified, so far, to show synergistic effects on some key properties required for applications such as contact lens.

The relationships among oxygen permeability, modulus, and tear strength with the amounts of bulky polysiloxanylalkyl acrylic monomers, such as TRIS, is also applicable to silicone hydrogels based

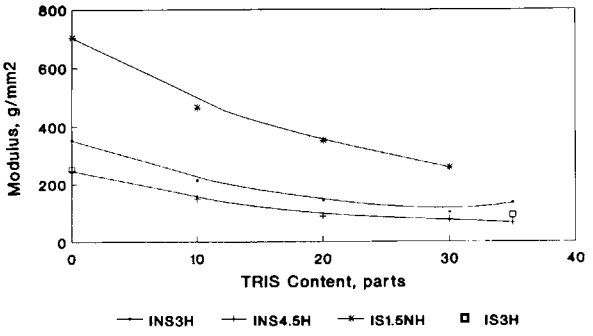


Figure 6 The relationship between tensile modulus and TRIS in hydrogels (NPG series).

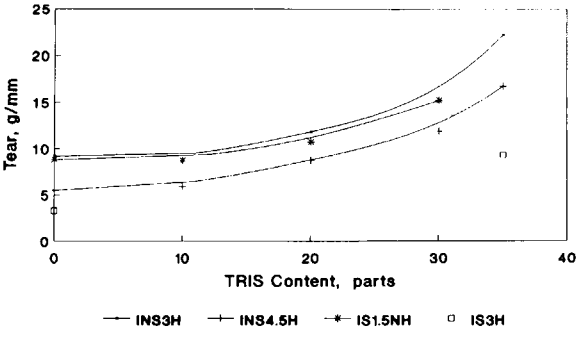


Figure 8 The relationship between tear strength and TRIS in hydrogels (NPG series).

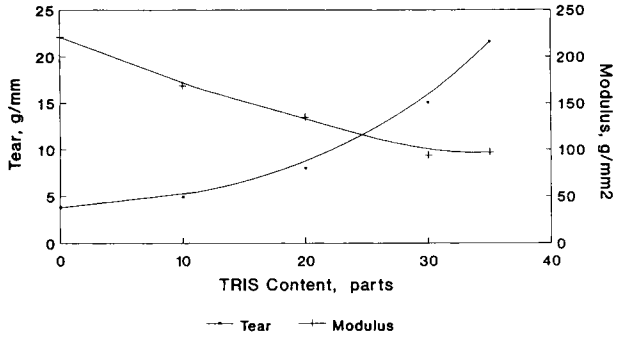


Figure 9 The relationship between tear strength/modulus and TRIS in hydrogel derived from IDS3H and DMA, with DMA at 30% by weight.

on methacrylate-capped polysiloxane prepolymers without any urethane linkage between the methacrylate and siloxane groups other than hydrocarbon.[19] In these situations, using TRIS also brought the benefits of improved monomer compatibility as well as optical quality the hydrogels derived.[19] Although the discussion in this article was limited to certain applications, using bulky polysiloxanylalkyl methacrylates in hydrogels targeted for other applications might prove useful as well.

CONCLUSION

When a bulky polysiloxanylalkyl acrylic monomer, such as TRIS, is used to replace a portion of a polysiloxane-based polyurethane prepolymer in forming silicone hydrogels, it helps maintain high oxygen permeability, lowers modulus, and increases tear strength, making the hydrogels useful for contact lenses.

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REFERENCES

1. Y. C. Lai, A. C. Wilson, and S. G. Zantos, in *Kirk Othmer Encyclopedia of Chemical Technology*, 4th ed., Wiley, New York, 1993, Vol. 7, pp. 192–218.
2. B. A. Holden, G. W. Mertz, and J. J. McNally, *Invest. Ophthalmol. Vis. Sci.*, **24,** 218 (1983).
3. B. A. Holden and G. W. Mertz, *Invest. Ophthalmol. Vis. Sci.*, **25,** 1161 (1984).
4. S. M. Allen, M. Fujii, V. Stannett, H. B. Hopffenberg, and J. L. Williams, *J. Membr. Sci.*, **2,** 153 (1987).
5. D. F. Burdick, J. L. Mishler, and K. E. Polmanteer, U.S. Pat. 3,341,490 (1967).
6. N. G. Gaylord, U.S. Pat. 3,808,178 (1974).
7. E. J. Ellis and J. C. Salomone, U.S. Pat. 4,152,508 (1979).
8. T. B. Harvey, U.S. Pat. 4,711,943 (1987).
9. N. Stoyan, U.S. Pat. 4,829,137 (1989).
10. S. Ichinohe, K. Isobe, Y. Tahaka, and K. Kakahashi, U.S. Pat. 4,594,401 (1986).
11. E. J. Ellis, U.S. Pat. 4,424,328 (1984).
12. E. J. Ellis, U.S. Pat. 4,604,479 (1986).
13. S. H. Chang, U.S. Pat. 4,182,822 (1980).
14. Y. C. Lai and L. J. Baccei, *J. Appl. Polym. Sci.*, **42,** 3173 (1991).
15. Y. C. Lai and L. J. Baccei, *J. Appl. Polym. Sci.*, **42,** 2039 (1991).
16. Y. C. Lai, R. M. Ozark, and E. T. Quinn, *J. Polym. Sci. Part A Polym. Chem.*, **33,** 1773 (1995).
17. Y. C. Lai, *J. Appl. Polym. Sci.*, **56,** 301 (1995).
18. I. Fatt, J. E. Rasson, and J. B. Melpolder, *Int. Contact Lens Clin.*, **14,** 389 (1987).
19. Y. C. Lai, *J. Appl. Polym. Sci.*, **56,** 311 (1995).

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