

Elastomeric Electron Beam-Cured Coatings: Structure-Property Relationships. I. Oligomer Structure

WADIDA ORABY and WILLIAM K. WALSH, *Department of Textile Chemistry, North Carolina State University, Raleigh, North Carolina 27607*

Synopsis

Mechanical properties of electron beam-cured films were studied as a function of oligomer structure and monomer diluent. In films cast from polyester acrylourethane oligomers, increasing the chain length between the two acrylate groups on each end resulted in a decrease in breaking strength from 7000 psi to 1000 psi in Young's modulus from 200,000 psi to 700 psi, and in glass transition temperature from 50 to -25°C , while the ultimate elongation increased from 20% to 210%. These properties were virtually independent of dose above 1 Mrad. The elongations were compared with literature values at equivalent degrees of crosslinking and found to fall within the range, but on the low elongation side of the distribution. It was speculated that the crosslinks' functionality would equal the average degree of polymerization of the double bond at each end of the oligomer, resulting in multirayed, star-shaped crosslinks with less flexibility than those with the usual functionality of 3 or 4, and methods for reducing this functionality were investigated. Addition of active monomers effected only minor change, but diethylaminoethyl acrylate was found to be very helpful in increasing the extensibility of these films considerably. This behavior can be explained by assuming that this monomer has a significant chain transfer constant, which should reduce the degree of polymerization of acrylic endgroups, producing a looser structure.

INTRODUCTION

The use of high-intensity radiation (electron beam, EB, and ultraviolet, UV) as an alternative to the thermal process in curing and polymerization of resins has shown rapid growth and wide acceptance over the past five years in many industrially important technological areas. This is due to a number of desirable features, such as increased productivity, savings in energy and floor space, and great reductions in solvent emissions with 100% reactive coating systems. Much of the recent progress in this field has been made possible by the introduction of new radiation curing materials and equipment. The technique usually involves the use of a reactive mixture compounded from polyunsaturated oligomer (MW 1000 and up), either by itself or, more often, in combination with active monomer to reduce the viscosity. The literature contains reviews of a variety of such systems.¹⁻³ One system frequently used in industry involves the use of oligomers capped at both ends with highly active acrylate groups, usually in combination with acrylate monomers.³ This system has been found to be highly responsive to radiation, which sets the film to a crosslinked structure at very high rates. W. R. Grace Co.⁴ uses a different approach, termed the ene/thiol system. Here, the oligomer is usually terminated with two or more of the less reactive allylic groups. These do not readily polymerize but are presumed to react at high rate by free-radical addition to polythiol agents (two or more thiol groups) to form a crosslinked structure.

All the above systems are known to proceed by a free-radical mechanism, but the 3M Company⁵ has recently introduced a new system that cures photochemically by a cationic mechanism. EB curing has been applied in industry for coating metal, wood, and paper where an extremely high degree of cured film extensibility is not required for most applications. However, in textile applications which are just beginning to be investigated, extensions at break of greater than 200% are necessary for practically all end uses.

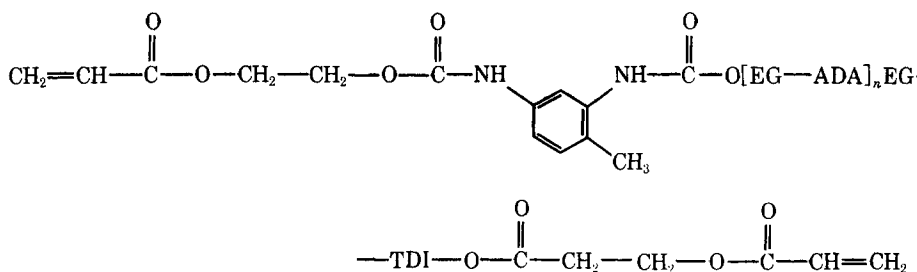
We have been studying the use of radiation in such applications as nonwoven fabric bonding,⁶ fabric coating,⁷ and pigment prints.⁸ It became apparent in the course of these studies that the mechanical properties of the cured films (in particular initial modulus and extensibility) are key factors in determining the extent to which radiation is to be of use in the textile industry. The effective short-gauge length of the resin as an adhesive between fibers makes it desirable that resin should be able to undergo moderately high extension in order that it may accommodate the relative movement of the fibers and yarns when a fabric is deformed.

In this study, working with well-defined, structurally characterized polyester acrylourethane oligomers allowed determination of relationships between oligomer structure and cured film properties. Further studies on additives and modifiers confirmed the relationships and produced an even wider range of properties.

EXPERIMENTAL

Materials

A series of reactive radiation-curable oligomers were synthesized and supplied by Thiokol/Chemical Division. Their simplified formula is given as the following:



where EG is ethylene glycol, ADA is adipic acid, and TDI is toluene diisocyanate. The molecular weight of the oligomers varied between 1000 and 6000 by increasing the molecular chain length between the two end acrylate groups. A list of other materials used in this study are given in Table I.

The viscosities of these systems were measured at 50°C with a Brookfield viscometer using a #4 spindle at 6 rpm.

TABLE I
List of Monomers and Other Additives

Name	Abbreviation	Supplier
Isodecyl acrylate	IDA	Union Carbide
Tergitol S-12 acrylate	TA	Union Carbide
N,N-Diethylaminoethyl acrylate	DEAEA	Union Carbide
Carbowax MPEG 550 acrylate	MPEGA	Union Carbide
Silicon Surfactant L-520 Dimethylaminoethyl methacrylate	DMAEMA	Alcolac Chemical
Hydroxyethyl methacrylate	HEMA	Alcolac Chemical
Tetrahydrofurfuryl methacrylate	THFMA	Sartomer
Tetrahydrofurfuryl acrylate	THFA	Sartomer
Pentaerythritol triacrylate	PETA	Celanese
1,6-Hexanediol diacrylate	HDDA	Celanese
Isobornyl acrylate	IBOA	Rohm & Haas
Tetraethylene Glycol Diacrylate	TEGDA	Celanese
N-Vinylpyrrolidone	V-pyrol	GAF
N-(1,1-Dimethyl-3-dimethyl aminopropyl)acrylamide	DMAPA	Lubrizol
N-(Isobutoxymethyl)acrylamide	IBMA	Amer. Cyanamide
Isooctyl thioglycolate	IOTG	Evans Chemetics
Tris(tetrahydrofurfuryl) phosphate	THFP	FMA
Carbon tetrabromide		Fisher Scientific
Methyl ethyl ketone		Fisher Scientific
Diethyl phosphite		Stauffer Chem.
Fluorad Surfactant FC-430		3M
2-Ethylhexyl acrylate	2EHA	Carbide & Carbon Chem.
Trimethylolpropane tris-3-mercaptopropionate	TMTMP	Evans Chemetics
Dibromopropyl Acrylate	DBPA	Borden Monomer Polymer Lab.

Processing

The molten oligomers or oligomer-monomer mixtures were cast on Mylar film using wire-wound rods. The film was then cured by an electron beam in a sealed polyethylene bag filled with nitrogen. The electron accelerator used was manufactured by High Voltage Engineering Corporation and has a maximum beam current of 20 mA. It was operated at 500,000 V for all experiments. Each irradiation was given in two passes, one on each side.

The percent gel of the cured film was determined by exhaustively extracting the uncrosslinked materials with trichloroethylene at room temperature.

Tensile Testing

Cured films were cut into 1.5 in. \times 0.5 in. strips using a die cutter. After conditioning for 24 hr at 70°F and 65% relative humidity, the specimen was clamped in an Instron testing machine, Model TT-B, with a jaw separation of 1 in. and extended at a rate of 1 in./min to failure, and the load extension diagram was recorded.

Glass transition temperatures of the cured films were measured on a Perkin-Elmer thermomechanical analyzer using the penetration mode at a heating rate of 10°C/min. The measurement was also made by dilatometry. No difference was observed between the two methods.

All testing was done on unextracted film.

RESULTS AND DISCUSSION

Pure Oligomer

Initial studies were made on pure oligomer with molecular weight as the independent variable. In this case the molten oligomers had to be cast on a heated plate due to their high viscosity (from 25,000 to over 100,000 cps). The molecular weight ranged between 1000 and 6000. The increase in molecular weight from 1000 to 4600 was obtained by increasing the polyester soft segment between the two end-acrylate groups. In the case of the 6000 molecular weight oligomers, both the urethane (hard) and the polyester segments were increased.

Reaction rates for five pure oligomers in the electron beam were determined by measuring the percent gel as a function of dose. The results are shown in Figure 1. All initial rates are extremely high and "level off" after 1 Mrad at fairly high yield. Both initial rates and final conversions decreased with oligomer molecular weight.

The kinetics of the reaction are not easily followed experimentally because of the insolubility of the crosslinked polymer, although more recently estimates were made of chain lengths of 22 and 78.5 using a different approach.^{9,10} The assumption of steady-state radical concentration is obviously not valid under these conditions, but the simple relationships derived from it can be used to qualitatively interpret the results in Figure 1.

The overall reaction rate R_p can be expressed as follows:

$$R_p = (k_p R_i^{1/2} / k_t^{1/2}) (M)$$

where R_i is the rate of initiation, (M) is the monomer (oligomer) concentration, k_p is the propagation rate constant, and k_t is the termination rate constant.

The degree of polymerization P_n may be written as

$$P_n = (k_p / k_t^{1/2} R_i^{1/2}) (M)$$

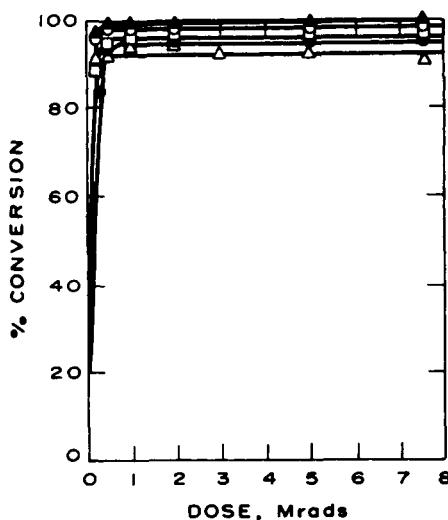


Fig. 1. Percent gel of oligomer as function of dose. MW: (▲) 1061; (○) 1953; (□) 3004; (●) 4600; (△) 6000.

One may speculate that the high reaction rate in the beginning is due to decrease in k_t resulting from the high viscosity of the oligomers and the early onset of gelation in such a bifunctional system. This effect is more pronounced in the lower molecular weight oligomers due to the high concentration of the double bonds. The very slow reaction after the initial rapid rise is due to the restricted mobility of the double bonds associated with the advanced degree of the overall reaction rate.

The low mobility during this slow reaction period is reflected by the elastic initial modulus of the film which reaches a surprisingly high value even at 0.25 Mrad and does not change with dose above 1 Mrad, as can be seen in Figure 2. The experimental values for modulus were quite reproducible, so the scatter in these points is presumably due to slight lot-to-lot variations in the oligomers. It may be mentioned here that it was difficult to obtain a good film from the neat 6000 molecular weight oligomer, because of its high viscosity and surface tension, and thus such film was not included in this discussion. The moduli at 5 Mrad are shown as a function of oligomer molecular weight in Figure 3. As can be seen, the lowest molecular weight oligomers give films of the highest modulus. The modulus drops significantly as the molecular weight increases, then levels off. The primary factor affecting the variation in the modulus with the molecular weight is the glass transition temperature of cured film, also shown in Figure 3. The low (1000) molecular weight oligomers produce films that are really different

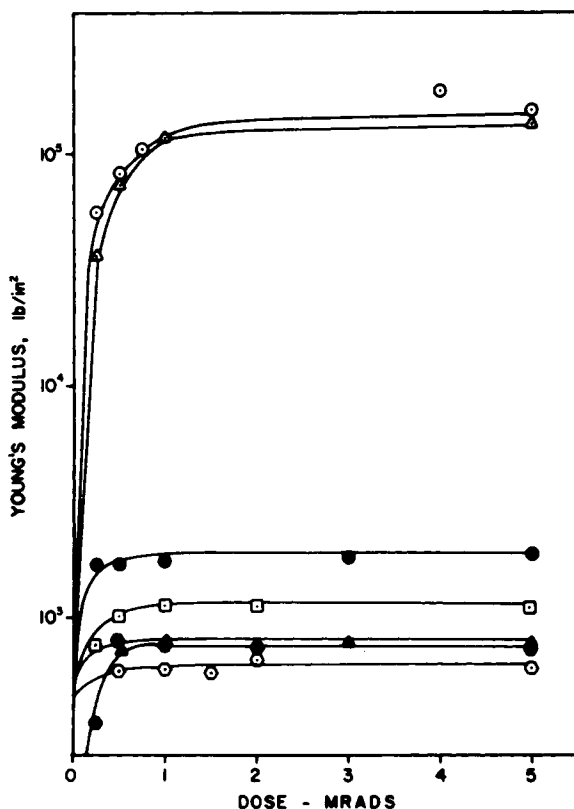


Fig. 2. Moduli of cured films as function of dose. MW: (○) 1082; (Δ) 1061; (□) 1953; (●) 2000; (○) 2890; (▲) 3004; (●) 4600.

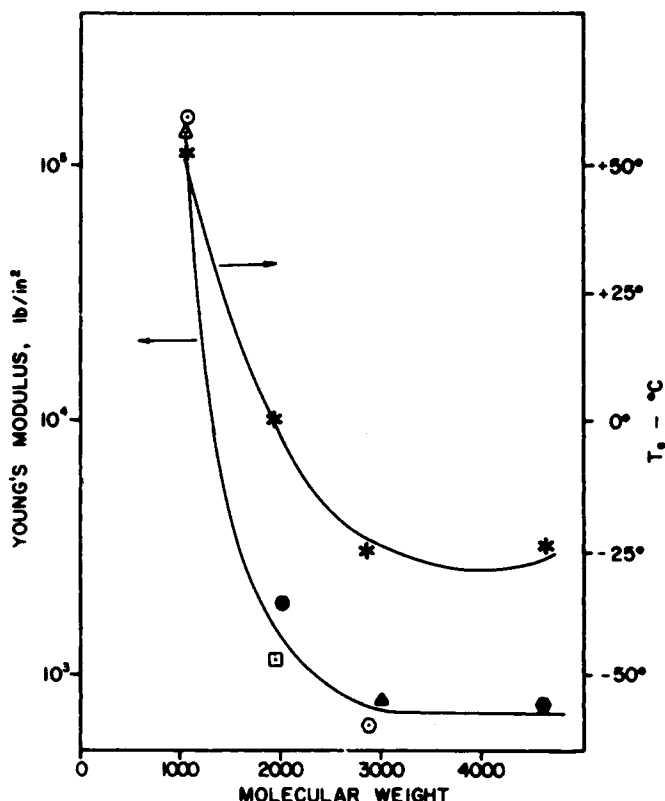


Fig. 3. Moduli and glass transition temperature as function of initial molecular weight, at 5 Mrad.

from others, in that their glass transitions are above room temperature. Both the breaking strength and the percent elongation at failure are shown in Figures 4 and 5 as a function of oligomer molecular weight.

The strength drops steeply as the molecular weight is increased, then levels off beyond a molecular weight of 2000. The percent elongation continues to increase almost linearly from 20% at a molecular weight of 1000 to 210% for a molecular weight of 4600.

The percentage swelling of films irradiated between 0.25 and 5 Mrad was measured using trichloroethylene solvent. The continuous slight decrease in swelling with increased dose indicates that there was further reaction even at high dose, a fact not obvious from the results on other physical properties. The decrease in percent swelling with increasing dose up to 5 Mrad was attributed to a slight increase in crosslinking. When plotting the modulus versus percentage swelling, Figure 6, it becomes evident that only in the soft films is the modulus practically independent of further crosslinking, while in stiff films (MW 1000) there is a continuous increase in modulus up to 5 Mrad. This behavior was found to be due to removal (by polymerization) of oligomer, which acts as a plasticizer in the unextracted films.

In application of polymeric materials to textiles, a reasonably high elongation at failure seems to be a requirement for practically all end uses. The two structural features of an elastomer that influence this property most are the

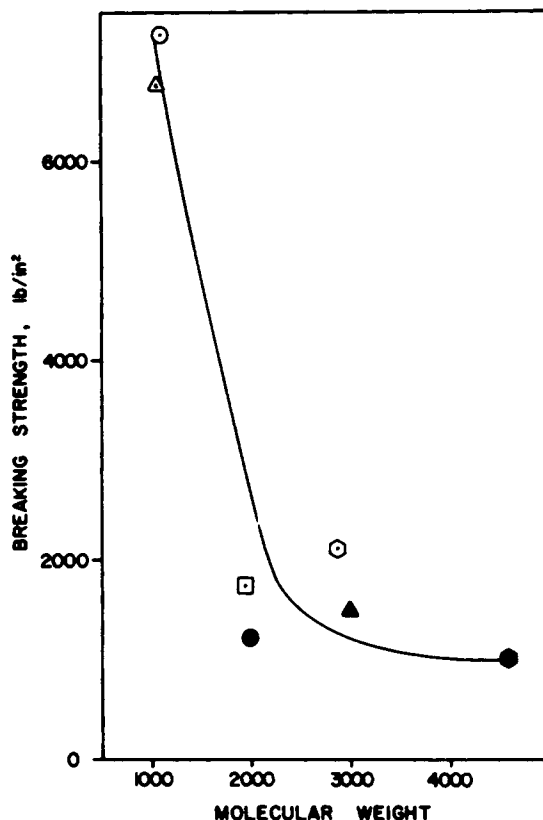


Fig. 4. Breaking strength as function of molecular weight, at 5 Mrad.

degree of crosslinking and the glass transition temperature (T_g). Kaible¹¹ summarized the work of Landel and Fedors¹² who examined this relationship in some detail and showed that the extension ratio (λ_b) at break is approximately proportional to the square root of the molecular weight of the chain between crosslinks (divided by density), in apparent agreement with the theory. At a given degree of crosslinking, as the test temperature is varied, the breaking elongation passes through a broad maximum at about 10 to 40°C above T_g , depending also of course on the rate of extension. Landel and Fedors¹² gathered data from a number of studies and correlated breaking elongation (maximized for temperature and extension rate) and molecular weight between crosslinks. All the data in their analysis fell within the limits shown in Figure 7, where the data for the oligomers in this study are also plotted, assuming that the oligomer molecular weight equals M_c . In comparison, the radiation-cured films fall within the range of their data, but near the low end of distribution.

There are several possible reasons that the elongations are not as high as they might be. First, the film properties (especially those from the low molecular weight oligomers) are not maximized as to test temperature and rate of extension. Second, although the samples were selected to eliminate visible flaws, minor flaws were certainly present and contributed to lower elongations. The most significant difference, however, lies in the fact that all elastomers in the literature have crosslinking functionality of 3 or 4 where only three or four molecular chains are

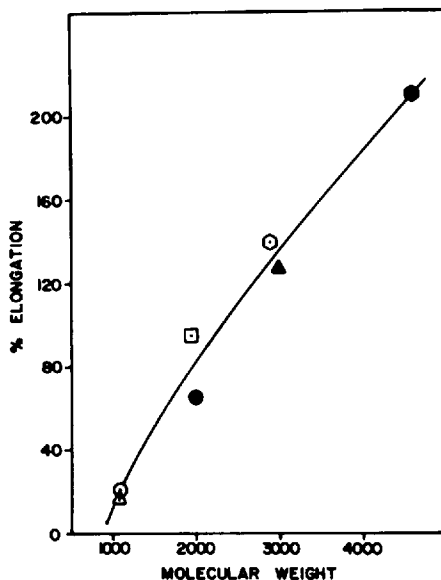


Fig. 5. Elongation at break as function of molecular weight, at 5 Mrad.

linked at each junction. It is known¹³ that a functionality of 3 produces more extensible films than a functionality of 4. In curing an oligomer by polymerizing the double bonds at each end, the average crosslink functionality would equal the average degree of polymerization of the double bonds. A chain length of even 10 to 20 would result in a multirayed, star-shaped crosslink (illustrated in Fig. 8), with less flexibility than the usual tetrafunctional cross-shaped link, and the effective molecular weight of chains between crosslinks may be much less than predicted.

Oligomer-Monomer Systems

From the above discussion it is apparent that the high viscosity of these oligomers and their tightly crosslinked structure are factors that limit their successful application to textile materials. Accordingly, an extensive study was made here on the effect of adding reactive monomers to oligomers of different molecular weight to reduce viscosity of the system. Furthermore, it was thought that copolymerizing the monomer with oligomer double bonds may serve to break up or smear this star-shaped crosslinking somewhat and may thus contribute to the flexibility and elongation.

A number of different candidate monomers were tried (listed in Table I). As expected, the addition of monomers decreased the viscosity substantially and made it possible to cast the films easily at room temperature.

The reactivities of some of these monomer-oligomer systems consisting of 75% oligomer to 25% monomer are shown in Figures 9 through 12. Others are reported elsewhere.⁸

From the results obtained, it is generally apparent that the response of these systems to electron beam radiation is comparable to that of neat oligomers. Some systems showed slightly higher response, e.g., systems containing V-pyrol and PETA, while others responded less readily, as in the case of THFMA and

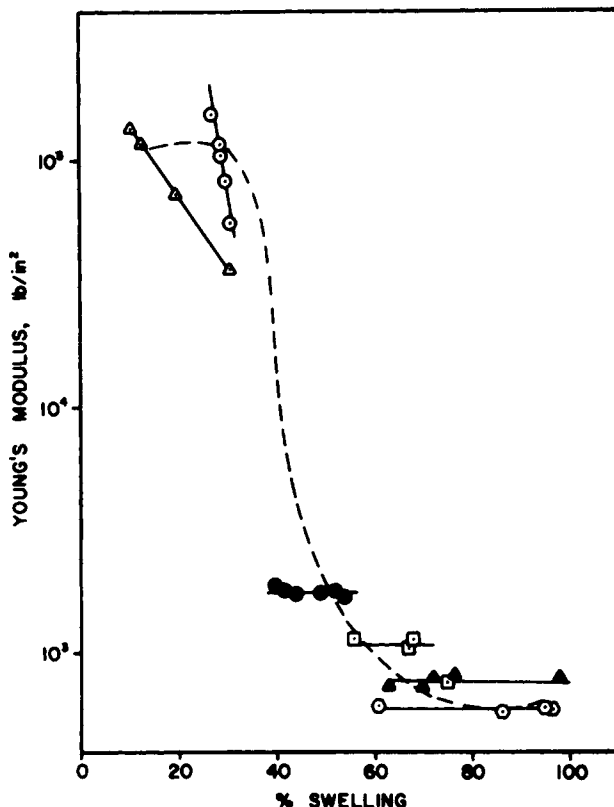


Fig. 6. Film moduli as function of swelling in trichloroethylene. MW: (○) 1082; (△) 1061; (□) 1953; (●) 2000; (○) 2890; (▲) 3004.

DEAEA. However, in all cases it was found that with any particular monomer, the reactivity of the system with oligomers of different molecular weight decreased with increasing oligomer molecular weight.

Although the exact reason for the effect of these monomers on the reactivity of these systems is not quite clear, it is evident that the greater the molecular unsaturation in the system (resulting either from the monomer or the oligomer), the greater the response of the system to ionizing radiation.¹⁴ Exception should be made here for V-pyrol, a monofunctional monomer that showed high reactivity. This observation was also made by others.¹⁵ In the particular case of DEAEA, the decrease in reactivities is likely due to its chain transfer character, as is discussed later.

In some systems the monomer proportion was increased up to 50%. As can be seen in Figure 13, increasing V-pyrol from 25% to 38% did not practically affect the reactivity, while 50% addition decreased the 9 percent conversion somewhat at low dose but reached high conversion (96%) at 2 Mrad.

On the other hand, increasing the addition of THFMA resulted in a retardation effect and even an inhibition of the reaction at low doses, as can be seen in Figure 14. Here an induction period is observed the length of which increases with increasing the percentage addition of the monomer in the system.

The relatively high reactivity of the above monomer, when present in small proportion with the oligomer, should be due to the relatively high viscosity of

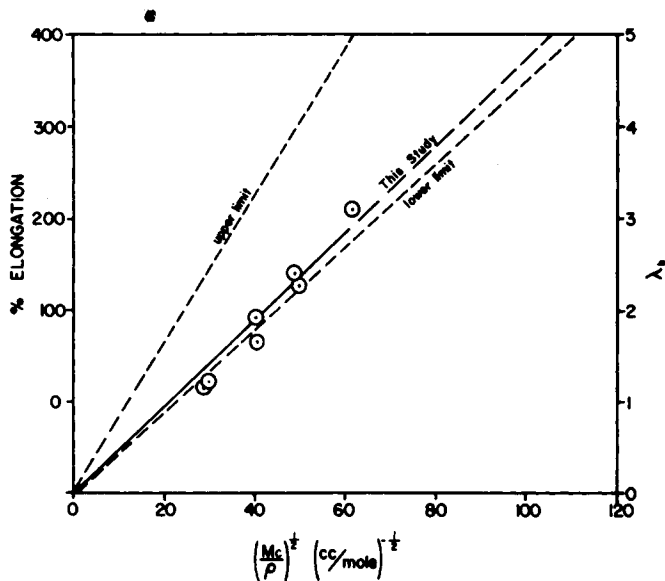


Fig. 7. Comparison of radiation-cured oligomers' elongation at break with other elastomers in the literature.

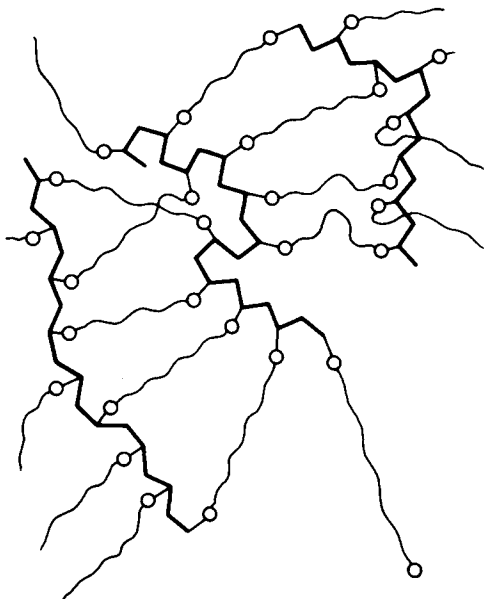


Fig. 8. Multirayed star-shaped crosslink structure.

the system combined with the early onset of gelation due to the polyfunctionality of the oligomer. This condition will enhance the copolymerization step relative to termination. As more monomer is added, the viscosity is decreased and the gel effect is delayed, leading to the observed retardation.

Several experiments were carried out on the effect of EB irradiation on neat, monofunctional monomers. Substantial (60%–90%) gel was obtained at 5 Mrad in nitrogen for IDA, TA, MPEGA, DMAPA, and 2EHA. No gel was found in

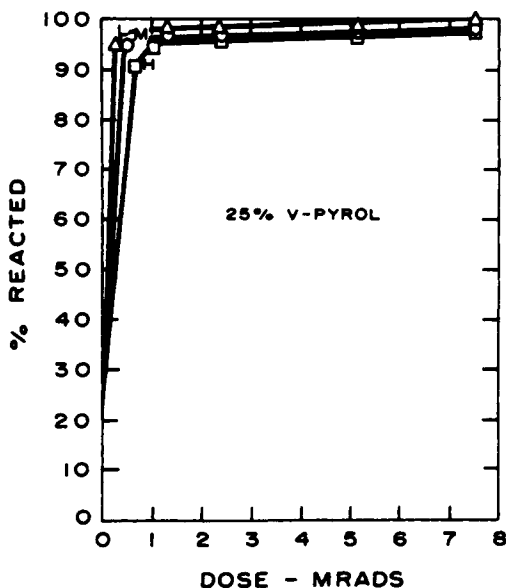


Fig. 9. Reaction rate of 25% V-pyrol in (L) 1082, (M) 2000, and (H) 3004 MW oligomers.

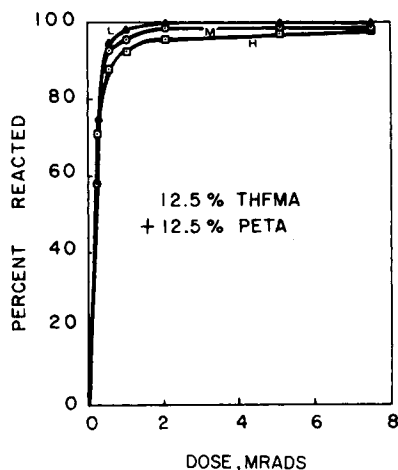


Fig. 10. Reaction rate of 12.5% THFMA + 12.5% PETA in (L) 1082, (M) 2000, and (H) 3004 MW oligomers.

the case of V-pyrol, THFMA, and DEAEA. The first group of acrylates should be predicted to crosslink from their structure.¹⁶ Evidently V-pyrol and THFMA do not fall into this category.

More studies have been made on other variables such as oxygen, dose rate, monomer volatility, stabilizer, etc. The results can be found elsewhere.⁸

Physical properties, namely, the breaking strength, Young's modulus, and percentage elongation, of films made of 75% oligomer and 25% monomer and cured at 5 Mrad are shown in Figures 15 through 18. It can be seen from these figures that, as is the case with neat oligomer, both the breaking strength and Young's modulus decreased and the percentage elongation increased as the molecular weight of the oligomer increased.

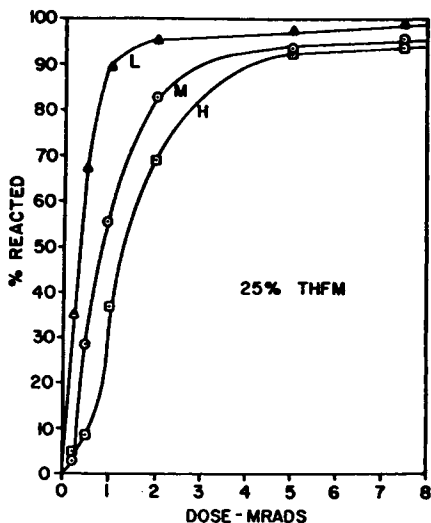


Fig. 11. Reaction rate of 25% tetrahydrofurfuryl methacrylate in (L) 1082, (M) 2000, and (H) 3004 MW oligomers.

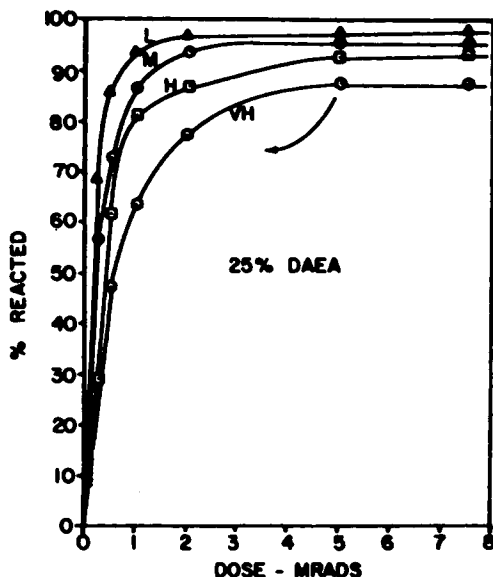


Fig. 12. Reaction rate of 25% diethylaminoethyl acrylate in (L) 1082, (M) 2000, (H) 3004, and (VH) MW oligomers.

PETA diluted with THFMA was found to be the most effective at enhancing the breaking strength of the film as well as its modulus while decreasing the percentage elongation as compared to the neat oligomer. This is to be expected because PETA monomer should increase the crosslink density. V-Pyrol was found to enhance both the breaking strength and modulus, while having little effect on the percentage elongation. THFMA was found to be almost without effect on the physical properties.

DEAEA had a remarkable effect on the extensibility of the films in that, by its addition to high molecular weight oligomer (4600), it was possible to obtain

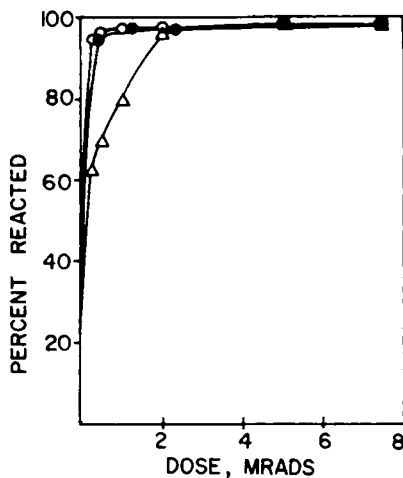


Fig. 13. Effect of V-pyrol concentration on reactivity of 2000 MW oligomers. (O) 25% V-pyrol; (●) 38% V-pyrol; (Δ) 50% V-pyrol.

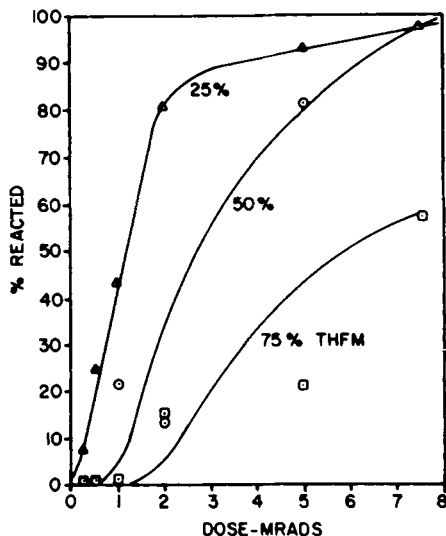


Fig. 14. Effect of tetrahydrofurfuryl methacrylate concentration on reaction of 1953 MW oligomer.

an elongation of 400% while maintaining breaking strength at about the same level as film made of pure oligomer. This behavior can possibly be explained by the assumption that DEAEA has a significant chain transfer constant, which should reduce the degree of polymerization of the acrylic endgroups. This should minimize the formation of multirayed shaped crosslinks (Fig. 8) producing a more loose structure. On the other hand, the DEAEA may also, by transfer, stop the growth of the copolymerizing chain at a very early stage, resulting in an increase in the percentage of extractable material. This explains the lower percentage conversion obtained with such systems.

In conclusion, it can be said that the oligomer structure is the backbone of the electron beam cured film properties. It is possible by changing the percent

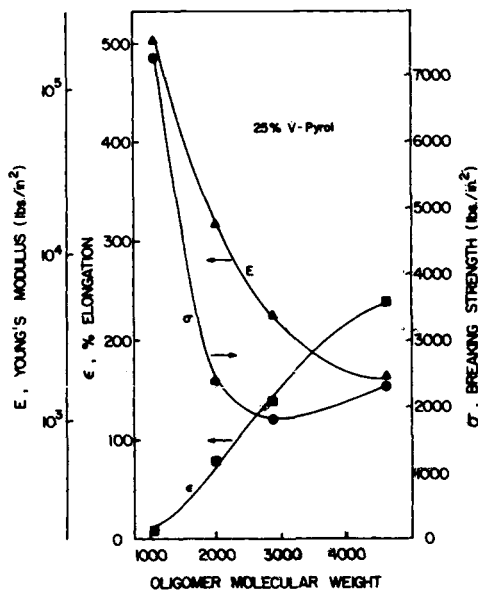


Fig. 15. Physical properties as function of oligomer MW.

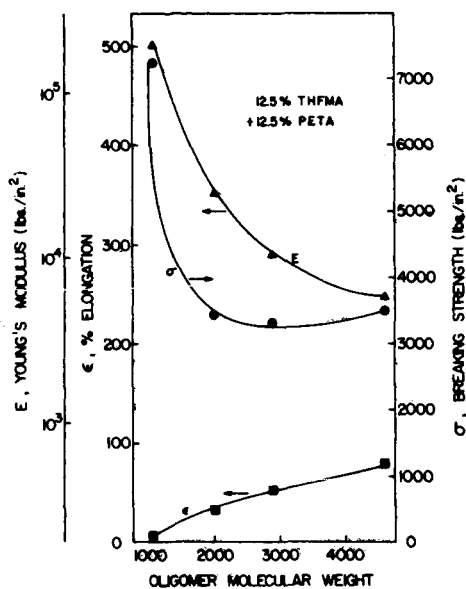


Fig. 16. Physical properties as function of oligomer MW.

unsaturation as well as the proportion of the hard and soft segment of these systems to obtain films that vary between glassy, stiff coatings and flexible elastomers. Curing these oligomers by polymerizing the double bonds at each end under the influence of electrons results in the formation of a multifunctional crosslinked structure that has a negative impact on the extensibility of the films.

Addition of 25% by weight of active monomers to these systems was found in general to have a minimal effect on film properties without changing their

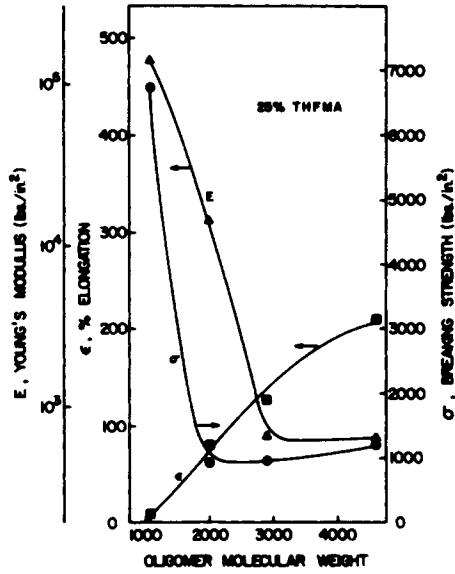


Fig. 17. Physical properties as function of oligomer MW.

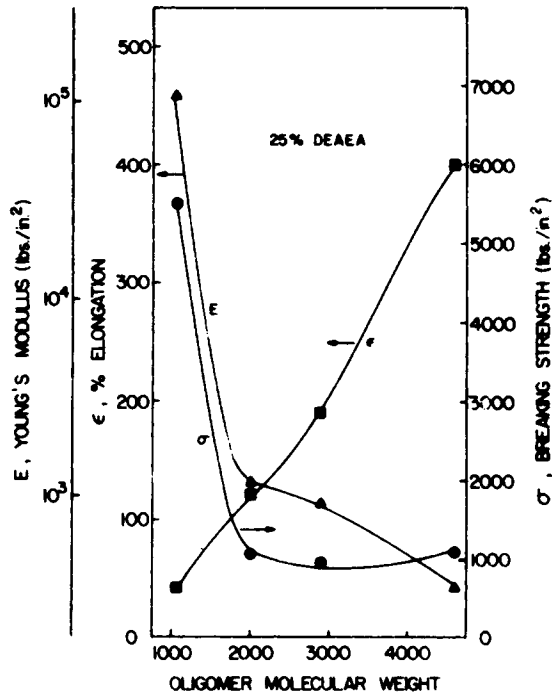


Fig. 18. Physical properties as function of oligomer MW.

complex crosslinking structure. Later investigations showed the use of mercaptofunctional chain transfer agents to be one way of cutting down the polyfunctionality of the system and was found to contribute in this way to the extensibility and toughness of the films. These are described in the next part of this paper.

References

1. S. H. Schroeter, "Ann. Rev. Mater. Sci., 5, 115 (1975).
2. A. Vrancken, *J. Chim. Peint.*, 73(1) 19 (1973).
3. T. F. Huemmer, *J. Radiat. Curing*, 1 (3), 9 (1974).
4. C. R. Morgan, F. Magmotta, and A. D. Ketley, *J. Polym. Sci., Polym. Chem. Ed.*, 15, 627 (1977).
5. *Radiat. Curing*, 3(4) (November 1976).
6. H. Chu, W. Oraby, E. Bittencourt, and W. K. Walsh, *J. Formed Fabric Ind.*, 6, (April 1977).
7. W. K. Walsh, K. Hemachandra, E. Bittencourt, W. Oraby, and B. S. Gupta, Proc. SME 3rd Radiation Curing Conf., Paper No. FC76-520, 1976.
8. W. K. Walsh et al., High Energy Radiation for Textile: Assessment of a New Technology, Final Report to NSF, RANN, on Grant GI43105, May 1974, April 1977.
9. S. S. Labana, *J. Polym. Sci.*, 8, 176 (1970).
10. C. C. Allen, W. Oraby, T. M. Hassain, E. P. Stahel, D. R. Squire, and V. T. Stannett, *J. Appl. Polym. Sci.*, 18, 709 (1974).
11. Kaeble, D. H., *Physical Chemistry of Adhesion*, Wiley, New York, 1971, p. 385.
12. R. F. Landel and R. F. Fedors, Proceedings of the 4th International Congress on Rheology, Part 2, E. H. Lee, Ed., Wiley, New York, 1965, p. 540.
13. L. C. Case, *Makromol. Chem.*, 37, 243 (1960).
14. C. C. Allen, W. Oraby, D. R. Squire, E. P. Stahel, and V. Stannett, *J. Macromol. Sci.-Chem. A*, 8(5), 965 (1974).
15. Lorenz, D. H., Tu, R., Azorlosa J., and Dwyer, W., *Proc. of 3rd Int. Rad. Curing Conf.*, FC 76-526, Sept. 28-30, 1976.
16. A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Interscience, New York, 1962.

Received June 26, 1978

Revised August 11, 1978