

# Photopolymerization of poly(tetramethylene ether) glycol diacrylates and properties of the obtained networks

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A series of poly(tetramethylene ether) glycol  $\alpha, \omega$ -diacrylates have been prepared from the corresponding hydroxy-terminated oligomers. The acrylation reaction, performed with acrylic acid in the presence of *p*-toluenesulfonic acid as a catalyst, allowed us to obtain oligomers with  $\bar{M}_n$  in the range 250–2000 and an acrylic functionality close to 2. The  $\bar{M}_n$  of the acrylated product was always lower than that of the starting oligomer, suggesting the occurrence of degradation reactions. These were attributed to an acidic hydrolytic attack on the oligomer chain. The oligomers were subjected to an ultra-violet light promoted curing process as thin films on glass substrates under  $N_2$  atmosphere. Complete acrylic double-bond conversion was obtained in all cases, with the exception of the oligomer with the lowest molecular weight. The thermal and mechanical properties of the networks were investigated by means of differential scanning calorimetry, thermomechanical analysis and dynamic mechanical thermal analysis (d.m.t.a.). Amorphous and rubbery materials were obtained with the exception of those from the oligomers of the highest molecular weight, which showed partial crystallinity. By means of thermal analysis and d.m.t.a.,  $T_g$  values were measured and correlated to the molecular weights of the oligomers used. In particular, the  $T_g$  values, as a function of the crosslinking density, agreed with those calculated by the Nielsen equation. Moreover, equilibrium swelling measurements in water were performed. The results obtained are discussed on the basis of Flory's theory and interpreted in terms of the solubility parameters and the crosslinking densities of the networks. Copyright © 1996 Elsevier Science Ltd.

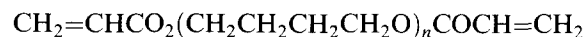
(Keywords: oligomers; acrylation; networks)

## INTRODUCTION

In a previous paper we studied the properties of polymeric films obtained from ultra-violet (u.v.) light cured poly(ethylene glycol) diacrylates<sup>1</sup> and investigated the relationships between the structure of the oligomers (molecular weight and acrylic functionality) and the properties of the networks obtained after the u.v.-initiated curing reaction. Moreover, preliminary studies on systems based on poly(propylene glycol) diacrylates were performed<sup>2</sup>.

Pursuing this research, we have taken into consideration poly(tetramethylene ether)  $\alpha, \omega$ -glycols as starting materials for preparing the corresponding diacrylate derivatives. The interest in these oligomers stems from their polarity characteristics, solubility and swelling behaviour. Moreover, such interesting properties of poly(tetramethylene ether) chains as their high flexibility, weathering stability and hydrolysis resistance are well known; they explain the wide use of these oligomers for the synthesis of block polyesters (trade name Hytrel)<sup>3</sup> and polyurethanes<sup>4</sup>.

The structure of the investigated oligomers can be given as



They were prepared by acrylating the corresponding  $\alpha, \omega$ -hydroxy oligomers having molecular weights in the range 250–2000.

The first compound of this series, tetramethylene glycol diacrylate, is a well-known compound, widely used as a reactive diluent in u.v. light curable systems<sup>5</sup>; the other oligomers have not so far been reported in the literature.

In this work, we investigate the preparation of these oligomers, their photopolymerization and some properties of the networks formed in the curing reaction.

## EXPERIMENTAL

### Materials

Tetramethylene glycol diacrylate (TMGDA) was supplied by Polysciences; it was used as received. The other poly(tetramethylene ether) glycol diacrylates (PTMEGDAs) were prepared by acrylation of the corresponding dihydroxy PTMEG oligomers supplied

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by Aldrich. Benzyl dimethyl ketal (Ciba-Geigy) was used as a photoinitiator. Solvents and reagents (Fluka) were distilled before use and stored under dry N<sub>2</sub>.

#### PTMEGDA oligomer synthesis

As an example, we describe the synthesis of PTMEGDA 650. PTMEG 650 (Aldrich) (10.0 g) was dissolved in benzene (80 cm<sup>3</sup>), 50 mg of hydroquinone and 2.44 cm<sup>3</sup> of acrylic acid (30% stoichiometric excess) was added and the mixture was heated for 2 h in a glass flask equipped with a reflux column and a Markusson head. *p*-Toluenesulfonic acid (0.5 g) was added and the mixture was refluxed for 9 h with azeotropic distillation of water. The reaction mixture was then treated with K<sub>2</sub>CO<sub>3</sub> in order to eliminate catalyst and free acrylic acid, stirred for 2 h at 40°C and filtered. The solvent was evaporated in a vacuum evaporator at 0.2 mmHg until a constant weight was reached. The yield of final product was 10.9 g. Complete removal of the solvent was checked by gas chromatography (g.c.). The product had an acrylic functionality of 1.91 and an acid number of 2.04 (number of milligrams KOH required to neutralize 1 g of sample).

A similar procedure was followed for the preparation of PTMEGDA 250, PTMEGDA 1000 and PTMEGDA 2000.

The acrylated products were named with a code indicating their structure, followed by a number denoting the molecular weight of the hydroxy-terminated oligomer used for the preparation of the diacrylated compound.

#### Curing procedure

The pure acrylate oligomers were mixed with 4% (w/w) of the photoinitiator and coated onto glass plates with a calibrated, wire-wound applicator to obtain a film thickness of about 100 μm. The coated plates were then irradiated with a medium pressure mercury lamp with a light intensity on the film of about 6 mW cm<sup>-2</sup>. For this process, the samples were held under a pure N<sub>2</sub> atmosphere (O<sub>2</sub> content < 20 ppm) in a small box equipped with a quartz window.

Free films were obtained by peeling them from the glass plates and completing the curing process by irradiating the other side of the film. The irradiation was continued until a constant double-bond conversion was reached (after about 20 s)<sup>1</sup>.

#### Analyses and film characterization

Fourier transform infra-red (FTi.r.) analysis was performed on the products coated on KBr discs, before and after u.v.-initiated curing, by means of a Bruker IFS 45 spectrometer.

$\bar{M}_n$  determinations were carried out with a Gonotec Osmomat 070-SA on CHCl<sub>3</sub> solutions at 37°C with benzil calibration.

The acrylic functionality was determined by means of the saponification method with an alcoholic 0.5 N KOH solution according to a procedure reported elsewhere<sup>6</sup>.

Viscosity measurements were performed with a Contraves Rheomat 15 viscometer at 20°C.

Gel permeation chromatography (g.p.c.) was performed with a Varian 5020 instrument on THF solutions at 25°C using two Styragel columns (Polymer Laboratories) with 50 and 100 Å pore sizes and a refractive index detector. Calibration was performed with polystyrene standards.

Film thicknesses were measured with a Minitest 3000 instrument (Elektrophysik Köln, Germany).

Differential scanning calorimetry (d.s.c.) and thermo-mechanical analysis (t.m.a.) were performed on a Mettler TA 3000 instrument equipped with a low temperature probe.

Dynamic mechanical thermal analysis (d.m.t.a.) was performed on a Polymer Laboratories instrument at 5 Hz in the tensile configuration.  $E_1$  and  $\tan \delta$  were measured as a function of temperature. The size of each specimen was about 20 × 40 × 0.1 mm.

Swelling values  $q$ , measured as the ratio of the final volume to the initial volume of the sample, were obtained through a 16 h water treatment at 25°C.

Gel contents were determined by measuring the weight decrease after a 16 h treatment with CHCl<sub>3</sub>.

## RESULTS AND DISCUSSION

#### Preparation of PTMEGDA oligomers

In Table 1, some data referring to the PTMEGDA oligomer properties are collected. In comparing the  $\bar{M}_n$  values of the PTMEGDAs with those of the corresponding PTMEG products, we see a decrease in  $\bar{M}_n$  which becomes greater with increasing oligomer molecular weight. At the same time, the acrylic functionality remains practically constant and near to two double bonds per molecule. The results in Table 1 indicate a

**Table 1** Properties of the PTMEGDA oligomers

Oligomer	$\bar{M}_n^a$	$\bar{M}_n^b$	Acrylic functionality	$T_f^c$ (°C)	Viscosity at 20°C (cP)	Acid number <sup>d</sup>
TMGDA	—	198	2.03	—	2	1.71
PTMEGDA 250	275	390	1.88	—	14	1.36
PTMEGDA 650	769	687	1.91	—	102	2.04
PTMEGDA 1000	1518	1051	1.90	—	228	4.41
PTMEGDA 2000	1952	1584	1.89	19.5	—	4.60

<sup>a</sup> PTMEG oligomer used

<sup>b</sup> Oligomer after acrylation

<sup>c</sup> By d.s.c.

<sup>d</sup> Number of milligrams KOH required to neutralize 1 g of sample

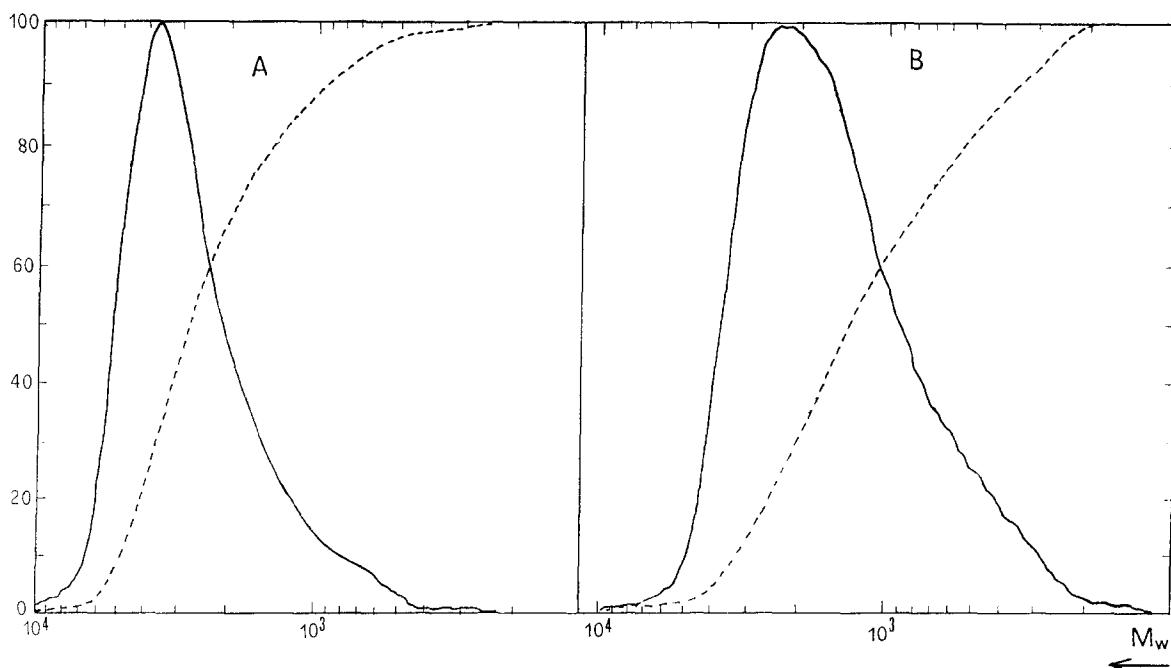


Figure 1 G.p.c. traces of (A)  $\bar{M}_w/\bar{M}_n = 1.80$  PTMEG 2000 and (B)  $\bar{M}_w/\bar{M}_n = 2.35$  the corresponding acrylated product

Table 2 Properties of u.v.-cured PTMEGDA oligomers

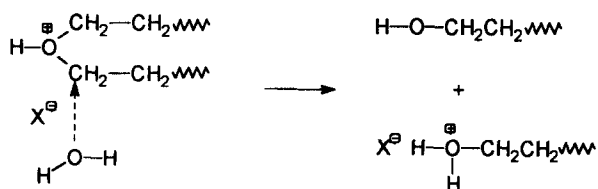
Oligomer	Double-bond conversion (%)	Gel content (%)	$T_g^a$ (°C)	$T_g^b$ (°C)	$T_g^c$ (°C)	Swelling value $q$
TMGDA	92.0	100.0	13	28	-	1.000
PTMEGDA 250	100.0	95.5	-12	-15	16	1.026
PTMEGDA 650	100.0	93.9	-65	-71	-	1.086
PTMEGDA 1000	100.0	93.8	-72	-81	-58	1.105
PTMEGDA 2000	100.0	96.3	-74	-83	-	1.148

<sup>a</sup> By d.s.c.

<sup>b</sup> By t.m.a.

<sup>c</sup> By d.m.t.a.

degradation reaction occurs during the acrylation process. In the synthesis of poly(ethylene glycol) diacrylates under similar conditions, there was no evidence of these reactions<sup>1</sup>. Similar reactions are, however, reported for PTMEG polymers in the presence of strongly acidic catalysts<sup>7,8</sup>. We can suggest an acidic hydrolytic attack on the oligomer chain with the formation of hydroxy groups according to



The hydroxy groups are then subjected to the acrylation reaction. The g.p.c. results shown in Figure 1 are in agreement with this explanation; moreover, they show that the molecular weight distribution increases during the acrylation reaction.

#### Properties of u.v.-cured PTMEGDA oligomers

Some properties of the u.v.-cured films obtained from

PTMEGDA oligomers are collected in Table 2. With the exception of the first member of the series, for all the oligomers a complete disappearance of the acrylic unsaturation was observed after the u.v.-initiated curing process. The incomplete acrylic double-bond conversion in the case of TMGDA can be attributed to the high crosslinking density of the network, which suppresses the mobility of the reactive species (vitrification)<sup>9</sup>. In Figures 2 and 3, the FTi.r. spectra of TMGDA and PTMEGDA 650 before and after the irradiation process are shown. The disappearance of the double-bond signals at 1635 and 1620  $\text{cm}^{-1}$  is evident, as well as a small amount of residual unsaturation present in the case of TMGDA.

Moreover, Table 2 shows the d.s.c., t.m.a. and d.m.t.a. results for the u.v.-cured films. All the oligomers give rise to completely amorphous products with low  $T_g$  which decreases on increasing the oligomer molecular weight. The only exception is PTMEGDA 2000: Figure 4 shows its d.s.c. thermogram compared with that of PTMEGDA 650. Figure 4 shows the presence of an endothermic peak at about 5°C that corresponds to a small fraction of crystalline structure (< 20%, calculated on the basis of the fusion enthalpy of PTMEG<sup>10</sup>). The

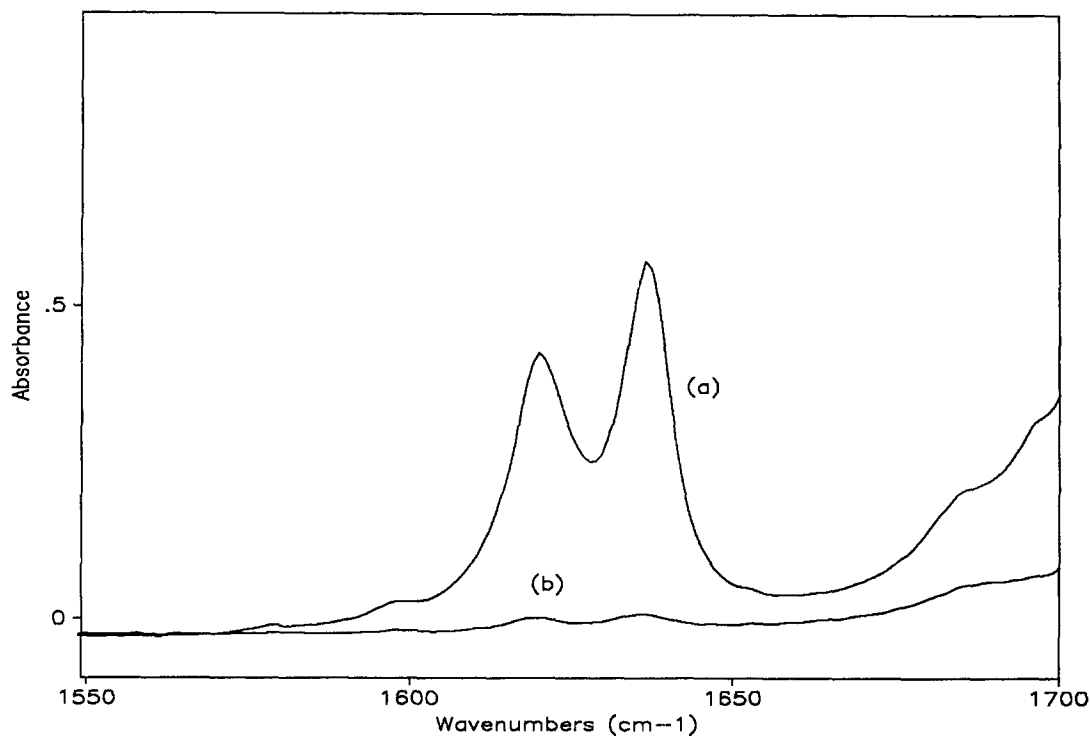


Figure 2 FTi.r. spectra of TMGDA film before (a) and after (b) u.v. irradiation

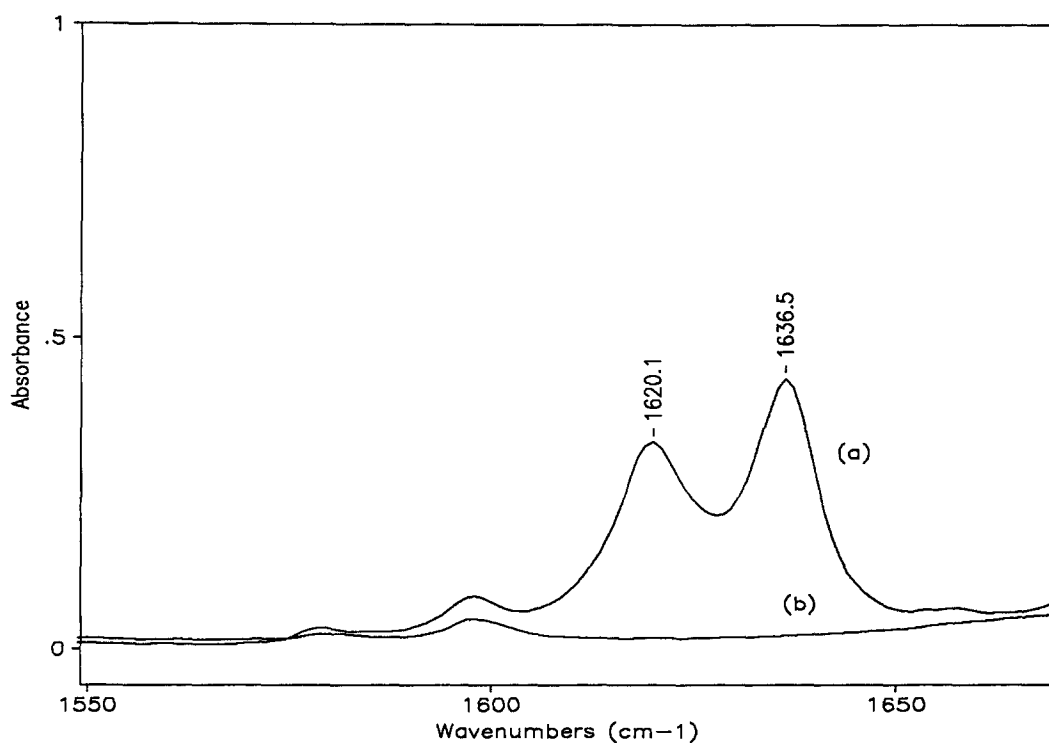


Figure 3 FTi.r. spectra of PTMEGDA 650 film before (a) and after (b) u.v. irradiation

t.m.a. thermogram of u.v.-cured PTMEGDA 650, shown in Figure 5, confirms the  $T_g$  value obtained via d.s.c.

A comparison of the thermomechanical properties of different poly(alkylene glycol) diacrylates is reported elsewhere<sup>11</sup>.

In Figure 6, the d.m.t.a. spectrum of u.v.-cured PTMEGDA 1000 is shown. It can be seen that  $\tan \delta$

reaches its maximum value at  $-58^\circ\text{C}$ , which can be considered as the  $T_g$  of the material. In the same temperature range, the storage modulus  $E'$  shows a sharp decrease, confirming the occurrence of the glass transition.

From the  $T_g$  values obtained by the different techniques (Table 2), it can be seen that those obtained by d.s.c. and t.m.a. are very similar, whereas those from

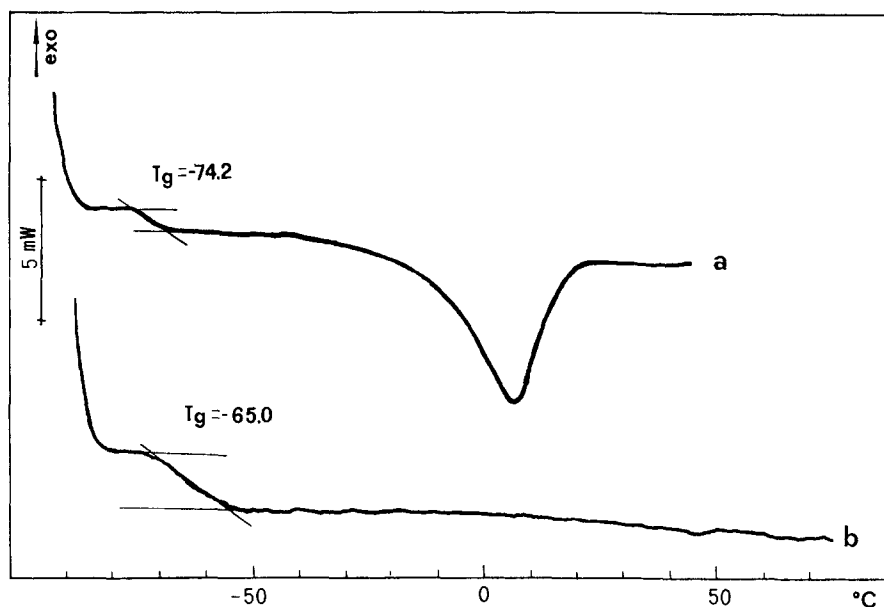


Figure 4 D.s.c. thermograms of u.v.-cured PTMEGDA 2000 (a) and PTMEGDA 650 (b)

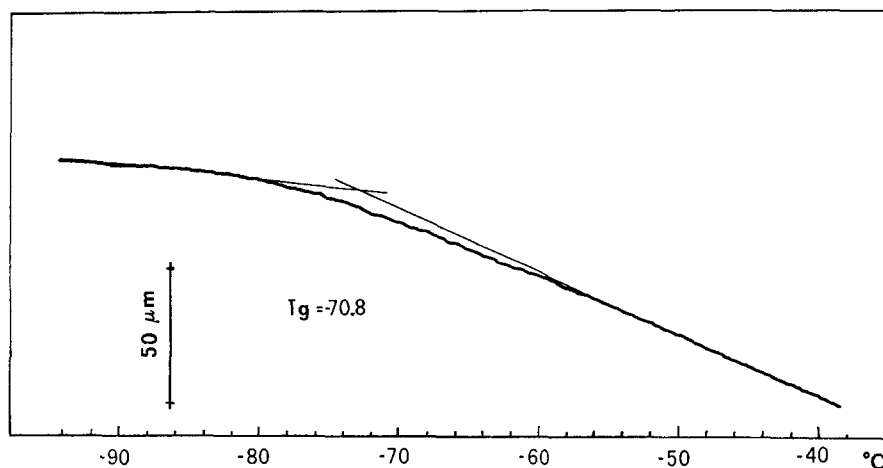


Figure 5 T.m.a. thermogram of u.v.-cured PTMEGDA 650 film

d.m.t.a. are higher. Similar results were obtained for the poly(ethylene glycol) diacrylates<sup>1</sup>. These results can be attributed to a frequency effect<sup>12</sup>.

The data for swelling in water (Table 2) are much smaller than those obtained for poly(ethylene glycol) diacrylates<sup>1</sup>, in agreement with the different solubility parameter values of the corresponding structures<sup>2</sup>.

#### Network characterization

As the double-bond conversion is practically complete for all the oligomers, we can calculate the crosslinking density  $\nu$  and the mean chain length between two crosslinks  $M_c$  value of the network formed in the u.v.-initiated curing process and correlate them with the measured properties. We have considered two network characteristics which are related to the crosslinking density, namely glass transition temperature and equilibrium swelling in water.

The  $T_g$  data reported in Table 2 show that the  $T_g$  decrease on increasing the molecular weight of the oligomer, i.e. on decreasing the network crosslinking density. Assuming that the mobility of the system is

almost unchanged on introducing the acrylic double bond, we can correlate the  $T_g$  variation with the length of the polymer chain between two acrylic double bonds. By plotting the  $T_g$  values obtained by t.m.a. as a function of the reciprocal value of the chain length  $M_c$ , we obtained a linear plot according to the Nielsen equation<sup>12</sup>, as shown in Figure 7. The  $T_g$  value extrapolated to  $1/M_c = 0$  is close to the  $T_g$  value of PTMEG<sup>13</sup>.

These results suggest that in spite of the possible network irregularities (incomplete acrylic functionality, cyclization reactions, network inhomogeneities<sup>9</sup>), the behaviour of the system investigated is rather regular and similar to that of the model network.

Further information about the network structure was obtained from equilibrium swelling measurements: according to Flory's theory<sup>14</sup>, swelling is related to the crosslinking density  $\nu$  and the polymer-solvent interaction parameter  $\chi$ . Water was chosen as a polar solvent; the parameter  $\chi$  was approximated by the solubility parameter, which gives an indication of the polarity of the network.

In Table 3, the solubility parameter values of

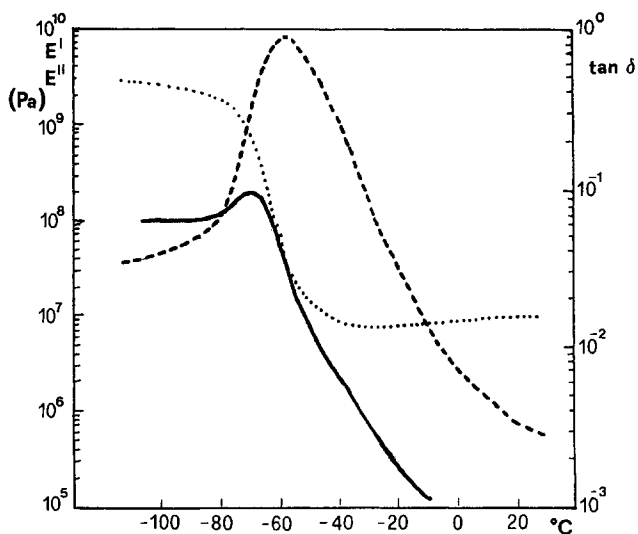


Figure 6 D.m.t.a. spectrum of u.v.-cured PTMEGDA 1000 film

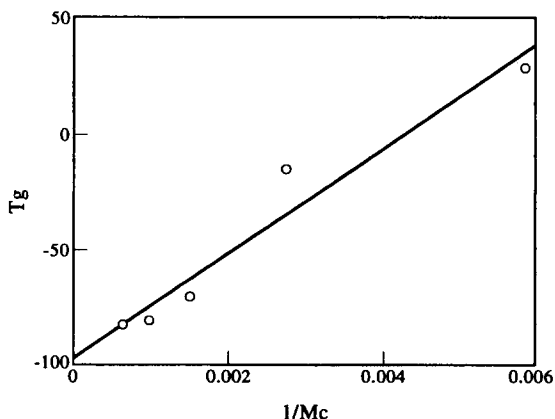


Figure 7  $T_g$  versus  $1/M_c$  for u.v.-cured PTMEGDA oligomers

PTMEGDA oligomers having different molecular weights are given. They were calculated according to a method given elsewhere<sup>15</sup> from the dispersion, polar and hydrogen bond contributions. The data show a small dependence of the solubility parameter on the oligomer molecular weight. Considering the measured equilibrium swelling values  $q$  for the different u.v.-cured PTMEGDA oligomers in water at 25°C

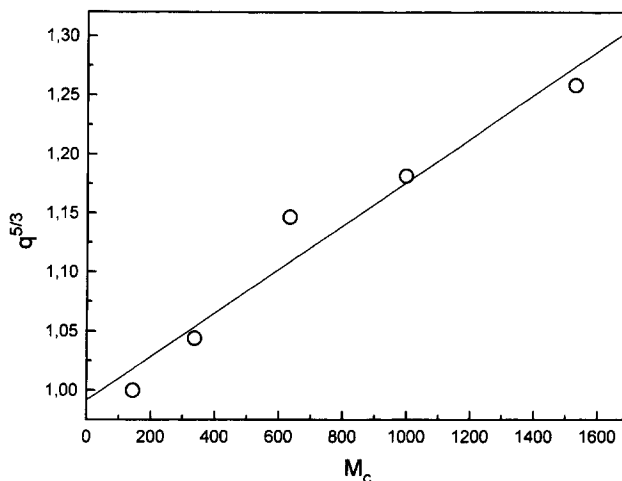


Figure 8 Swelling value ( $q^{5/3}$ ) versus  $M_c$  for PTMEGDA oligomers

(Table 2), we see a clear increase in  $q$  as a function of the oligomer molecular weight. As the solubility parameter is practically constant, the change in  $q$  has to be attributed mainly to a decrease in the network crosslinking density. The experimental data, processed according to the simplified Flory equation<sup>14</sup>, are plotted in Figure 8 and show a good agreement with the theoretical model.

### CONCLUSIONS

During the preparation of PTMEGDA oligomers, a decrease in molecular weight was found, the acrylic functionality remaining constant. This trend was attributed to a hydrolytic attack on the oligomer chain. The photopolymerization reaction led to a complete disappearance of the acrylic double bonds; thus, the network crosslinking density could be correlated to the oligomer molecular weight. The network properties were similar to those of the proposed model. In fact, a linear correlation of the  $T_g$  values of the u.v.-cured networks with  $1/M_c$  was evident, in good agreement with the Nielsen equation. Moreover, since the solubility parameters were practically independent of the molecular weight, the swelling in water of the networks could be related to their crosslinking density, as suggested by Flory's theory.

Table 3 Solubility parameters for PTMEGDA oligomers as a function of molecular weight

$n^a$	$V^b$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$\delta_d = \frac{\sum F_{di}}{V}$ ( $\text{J}^{1/2} \text{cm}^{-3/2}$ )	$\delta_p = \sqrt{\frac{\sum F_{pi}^2}{V}}$ ( $\text{J}^{1/2} \text{cm}^{-3/2}$ )	$\delta_h = \sqrt{\frac{\sum E_{hi}}{V}}$ ( $\text{J}^{1/2} \text{cm}^{-3/2}$ )	$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2}$ ( $\text{J}^{1/2} \text{cm}^{-3/2}$ )
1	198	19.93	5.03	7.78	15.91
4	414	14.73	2.93	7.12	16.62
9	774	15.50	1.95	6.82	17.05
14	1134	15.78	1.55	6.71	17.22
18	1422	15.91	1.36	6.66	17.30
28	2142	16.07	1.08	6.59	17.40
$\infty$					18.47

<sup>a</sup> Number of tetramethylene ether units in the oligomer

<sup>b</sup> Molar volume

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## REFERENCES

- 1 Priola, A., Gozzelino, G., Ferrero, F. and Malucelli, G. *Polymer* 1993, **34**, 3653
- 2 Priola, A., Gozzelino, G., Ferrero, F. and Malucelli, G. *Prog. Org. Coat.* 1993, **22**, 301
- 3 Wolfe Jr, J. R. *Adv. Chem. Ser.* 1979, **176**, 126
- 4 Lorty, J. J. and Gardlund, Z. G. *J. Appl. Polym. Sci.* 1981, **26**, 3657
- 5 Pappas, S. P. (Ed) 'UV Curing: Science and Technology', Vols 1 and 2, Technology Marketing Corporation, Stanford, CA, 1978 and 1985
- 6 Riddle, E. H. 'Monomeric Acrylic Esters', Reinhold, New York, 1954, p. 167
- 7 Dreyfuss, P. and Dreyfuss, M. P. *Adv. Chem. Ser.* 1969, **91**, 335
- 8 Dreyfuss, P., Dreyfuss, M. P. and Pruckmayr, G. in 'Encyclopedia of Polymer Science and Engineering' (Eds H. Mark, N. Bikales, C. Overberger and G. Menges), Vol. 16, Wiley-Interscience, New York, 1989, p. 649
- 9 Kloosterboer, J. G. *Adv. Polym. Sci.* 1987, **84**, 1
- 10 Wunderlich, B. 'Macromolecular Physics', Vol. 3, Academic Press, New York, 1980
- 11 Priola, A., Bongiovanni, R., Gozzelino, G., Ferrero, F. and Malucelli, G. *Makromol. Chem. Macromol. Symp.* 1995, **93**, 195
- 12 Nielsen, C. E. 'Mechanical Properties of Polymers and Composites', Vol. 1, Dekker, New York, 1994
- 13 Lehmann, J. and Dreyfuss, P. *Adv. Chem. Ser.* 1979, **176**, 587
- 14 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953, p. 577
- 15 Van Krevelen, D. W. 'Properties of Polymers', Elsevier, Amsterdam, 1976, p. 141