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Evaluation of the network parameter in aliphatic poly(urethane dimethacrylate)s by dynamic thermal analysis

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Abstract

The dicarbamates obtained from monomethacrylates of oligoethylene glycols and aliphatic diisocyanates were polymerised free radically to form crosslinked polymers consisting of primary chains, crosslinks and pendant side chains bearing unreacted methacrylate groups. The polymers were examined by dynamic mechanical thermal analysis (DMTA) to yield values of glass transition temperature and storage modulus. The latter enabled the network parameters for individual polymers to be evaluated. These have been found to be low when compared with molecular weights of the monomers and can be attributed to intermolecular interactions between the pendant chains and the crosslinks involving urethane linkages. This finding is supported by the ^{1}H NMR experiments on monomers in solution. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(urethane dimethacrylate); Network parameter; Dynamic mechanical thermal analysis

1. Introduction

Many important, modern synthetic materials are based on polymeric networks or crosslinked polymers. The former results from step-growth polymerisations of multifunctional monomers whereas the latter may be obtained either by performing chemical crosslinking of pre-formed linear macromolecules or by crosslinking chain reactions, i.e. by addition copolymerisation of a monofunctional monomer with a difunctional one [1].

When describing both polymeric networks and crosslinked polymers, the basic quantity used is the so called the network parameter (M_c), defined as the number-average molecular weight between branch points (junction points) [2]. In crosslinked polymers we can distinguish primary chains and crosslinks, and thus M_c relates to the segment of primary chain between two crosslinks [1]. The mole fraction of these chain repeating units which are crosslinked, i.e. crosslink density (q), relates M_c directly to the molecular weight of the repeating unit, in an addition polymer, to that of a monomer (MW) [1]:

$$M_c = \frac{MW}{q} \tag{1}$$

A particular case of crosslinking reactions was developed for dental restorative materials. Due to clinical requirements (minimisation of both polymerisation shrinkage and leachable residual monomer content), dental systems employ almost exclusively dimethacrylates having molecular weights of the order of a few hundreds, which polymerise when irradiated or via a chemical curing mode, to form a network [3].

Conversion of double bonds in dental restorative materials is never complete because of immobilisation, gelation, vitrification or steric isolation [4]. These molecules which have been incorporated into the polymer by one double bond only form pendant side chains, which act as permanent plasticisers [3]. Thus, cured dental materials may be considered to be built from primary chains formed by polymerisation of one of the double bonds of the dimethacrylates, crosslinked by those molecules in which both C=C bonds have reacted.

The experimental elucidation of the structure of a cured dental system is a rather difficult task. First of all, the binders employed in dentistry consist of mixtures of at least two dimethacrylate monomers differing in both chemical structure and molecular weight. In addition to the binders, dental composites contain particles of inorganic fillers which are bonded (during curing) to the organic matrix by silane coupling agents [3]. Therefore, to simplify the problem, we selected a more uniform model system,

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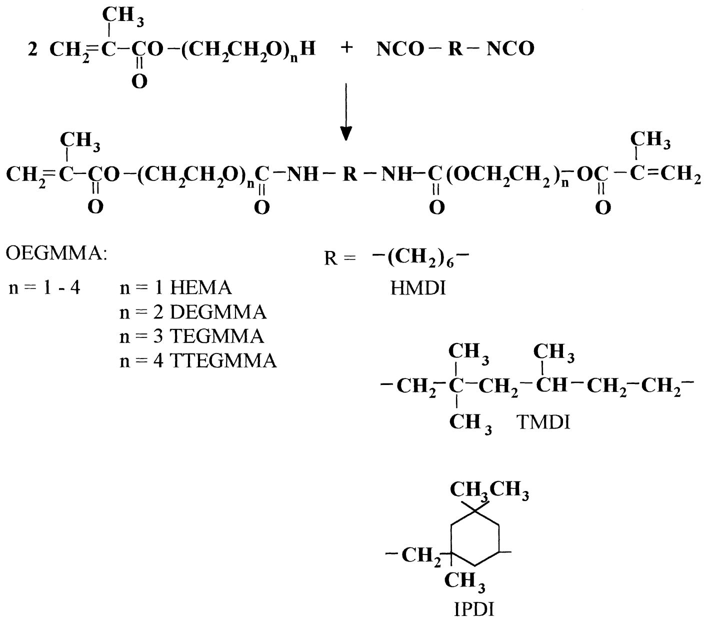

Fig. 1. The monomers.

namely the polymers of a previously synthesised homologous series of urethane–dimethacrylate monomers [5,6]. These monomers include dicarbamates obtained from oligoethylene glycol monomethacrylates (OEGMMA) and hexamethylene-1,6-diisocyanate (HMDI) [5] or 2,2,4(2,4,4)-trimethylhexyl-1,6-diisocyanate (TMDI) [6]. Additionally, we have synthesised an analogous series of monomers based on isophorone diisocyanate (IPDI). The structures of the monomers are given in the Fig. 1.

2. Experimental

2.1. Materials

DEG (diethylene glycol, POCh), DEGDMA (diethylene glycol dimethacrylate, Aldrich), TTEG (tetraethylene glycol, Fluka), MMA (methyl methacrylate, technical grade), HEMA (2-hydroxyethyl methacrylate, Sigma), IPDI (isophorone diisocyanate, Aldrich), DBTDL (dibutyltin dilaurate, Fluka), HQ (hydroquinone, POCh), HQME (hydroquinone monomethyl ether, Fluka) and PTZ (phenothiazine, Aldrich) were used as received. TEG (triethylene glycol, technical grade) was distilled under vacuum.

Potassium carbonate (anhydrous, POCh) was dried for few hours before use at 120°C. BPO (benzoyl peroxide, POCh) was purified by dissolving in chloroform and subsequent precipitation with methyl alcohol.

2.2. NMR measurements

^{1}H NMR spectra were recorded with the aid of UNITY/INOVA 300 MHz (Varian) spectrometer using $CDCl_3$ as a solvent and TMS as an internal reference.

2.3. Synthesis of monomethacrylates

2.3.1. Preparation of diethylene glycol monomethacrylate (DEGMMA)

DEG (59.5 g, 0.56 mol) and DEGDMA (135.8 g, 0.56 mol) of admixed with 5.78 g of K_2CO_3 (catalyst) and 68 mg of PTZ (inhibitor) were refluxed for 3 h in 180 cm^3 toluene. After cooling and filtering, the solution was washed twice with 270 cm^3 of distilled water. The aqueous layers were combined and then extracted with two portions of chloroform, 180 cm^3 each. The extracts were combined and dried overnight with anhydrous sodium sulphate. The chloroform was then removed under reduced pressure with a rotary evaporator. The crude product (64.9 g, 33.3% yield) was admixed with 7 mg of PTZ (inhibitor) and distilled under vacuum (0.02 kPa), taking the fraction boiling at 100–120°C as the main product with final yield of 11%.

^{1}H NMR: methacrylic protons at $\delta = 6.14$ (s, 1H), 5.59 (s,1H) and 1.95 ppm (s, 3H); CH_2OCO, $\delta = 4.32$ ppm (t,2H); oxyethylene protons $\delta \approx 3.6$–3.8 ppm (m, 6H); OH, $\delta \approx 2.6$ ppm (t, 1H). The multiplet of low intensity at $\delta \approx 1.2$ ppm originates from oligomeric side-products formed [7]; the fraction of the latter was estimated to be about 0.02.

2.3.2. Preparation of tri- and tetraethylene glycol monomethacrylates (TEGMMA, TTEGMMA)

TEG (112.6 g, 0.75 mol) and MMA (100 g, 1 mol) of admixed with 17.0 g of K_2CO_3 (catalyst) and 106 mg of HQ (inhibitor) were refluxed for 3 h in 414 cm^3 of toluene using a short Vigreux column equipped with a distillation head. The distillate (total amount ca 50 cm^3) was taken off at a moderate rate. After cooling, the reaction mixture was filtered and washed twice with distilled water in 2:1 volume ratio. Combined aqueous layers were then extracted twice with chloroform in 3:1 volume ratio. After evaporation of chloroform, the crude product (38% yield with respect to the glycol) was distilled under vacuum (0.2 hPa), taking the fraction boiling at 110–130°C as the main product with a final yield of about 13%.

The ^{1}H NMR spectrum of TEGMMA is identical to that of DEGMMA with an additional signal of central oxyethylene unit at $\delta = 3.68$ ppm (s, 4H). The fraction of oligomeric side-products was estimated to be about 0.04.

An analogous synthesis was performed starting with 145.7 g of TTEG to obtain monomethacrylate of tetraethylene glycol (TTEGMMA) with yields of crude product and of pure material of 52 and 22%, respectively.

The ^{1}H NMR spectrum of TTEGMMA is identical with that of TEGMMA except for the intensity of the signal of central oxyethylene units at $\delta = 3.68$ ppm which corresponded to 8H.

The fraction of oligomeric side-products was estimated to be about 0.05.

2.4. Syntheses of dicarbamates

2.4.1. Bis-(5-methyl-4-oxo-3-oxa-5-hexenyloxy)-N,N′-isophoronyl dicarbamate (HEMA/IPDI)

HEMA (65.1 g, 0.5 mol) admixed with DBTDL (36 mg, 0.03% w/w, catalyst) and 60 mg of HQME (500 ppm, inhibitor) was heated to 40°C in a three-neck flask equipped with a mechanical stirrer, a thermometer and a dropping funnel. Later, 55.6 g (0.25 mol) of IPDI was added dropwise for 1 h while maintaining the temperature at 50°C. Stirring was continued for 3 h and finally the mixture was left to stand overnight in the drying oven at 40°C. The product appeared to be a viscous, transparent and colourless resin.

Formation of dicarbamate was confirmed by ^{1}H NMR. Here, two broadened signals, a triplet at $\delta \approx 4.9$ ppm and a doublet at $\delta \approx 4.6$ ppm, each of the intensity corresponding to 1H, can be assigned to NH protons neighbouring (spin–spin coupling observed) to isophoronyl methylene and methine groups. The latter exhibited a series of broadened multiplets at $\delta \approx 3.9$–2.9 ppm, among which the most visible one is the doublet at $\delta = 2.93$ ppm, corresponding to NCH_2 group in its dominant isomeric form.

Other evidence for formation of the product is the collapse of the oxyethylene signals to the broadened singlet at $\delta = 4.31$ ppm; HEMA has two triplets at $\delta = 4.29$ and 3.87 ppm.

The remaining methylene and methyl groups of isophoronyl ring give a strongly coupled pattern at $\delta \approx$ 1.9–0.8 ppm, whereas the methacrylic protons exhibit the same chemical shifts as for the monomethacrylates.

2.4.2. Bis-(8-methyl-7-oxo-3,6-dioxa-8-nonenyloxy)-N,N′-isophoronyl dicarbamate (DEGMMA/IPDI)

The synthesis was performed in an analogous way to that of HEMA/IPDI starting from 38.4 g (0.22 mol) of DEGMMA and 24.4 g (0.11 mol) of IPDI in the presence of 20 mg of DBTDL.

The ^{1}H NMR spectrum differs with respect to that of HEMA/IPDI in the oxyethylene region. Four narrow multiplets of equal intensities corresponding to 4H each, are visible and can be assigned to four methylene group adjacent to the ester bond at $\delta = 4.31$ ppm; the urethane bond at $\delta = 4.21$ ppm, and the ether oxygen at $\delta = 3.77$ and 3.70 ppm.

2.4.3. Bis-(11-methyl-10-oxo-3,6,9-trioxa-11-dodecenyloxy)-N,N′-isophoronyl dicarbamate (TEGMMA/IPDI)

The synthesis was performed in an analogous way starting from 28.3 g (0.130 mol) of TEGMMA and 14.4 g (0.065 mol) of IPDI in the presence of 13 mg of DBTDL.

The ^{1}H NMR spectrum of the product, in comparison to that of DEGMMA/IPDI, contains an additional signal from the central oxyethylene unit at $\delta = 3.70$ ppm (s, 8H).

2.4.4. Bis-(14-methyl-13-oxo-3,6,9,12-tetraoxa-14-pentadecenyloxy)-N,N′-isophoronyl dicarbamate (TTEGMMA/IPDI)

The synthesis was performed in an analogous way starting from 32.0 g (0.122 mol) of TTEGMMA and 13.6 g (0.061 mol) of IPDI in the presence of 14 mg of DBTDL.

The ^{1}H NMR spectrum of the product is same as for TEGMMA/IPDI, except for the singlet of the central oxyethylene units, which has an intensity corresponding to 16H.

2.5. Polymerisation

Monomers were mixed with 1% by weight of BPO and polymerised in Petri dishes placed in a drying oven under nitrogen, raising the temperature gradually from 50 to 90°C over 24 h.

2.6. Dynamic mechanical thermal analysis

DMTA measurements were performed on $2 \times 5 \times 50$ mm samples using a Polymer Laboratories MK II apparatus at a frequency of 1 Hz. T_g and E' values were read off directly from variations of tan δ with temperature and log E' with temperature.

3. Discussion

The products of the polymerisation reactions investigated can be formally considered as crosslinked polymers, similar to those formed by addition copolymerisation of mono- and difunctional monomers, but obtained in the absence of a monofunctional one.

In order to find a relationship connecting the network parameter (M_c), the monomer molecular weight (MW), the conversion of double bonds (α) and the crosslink density

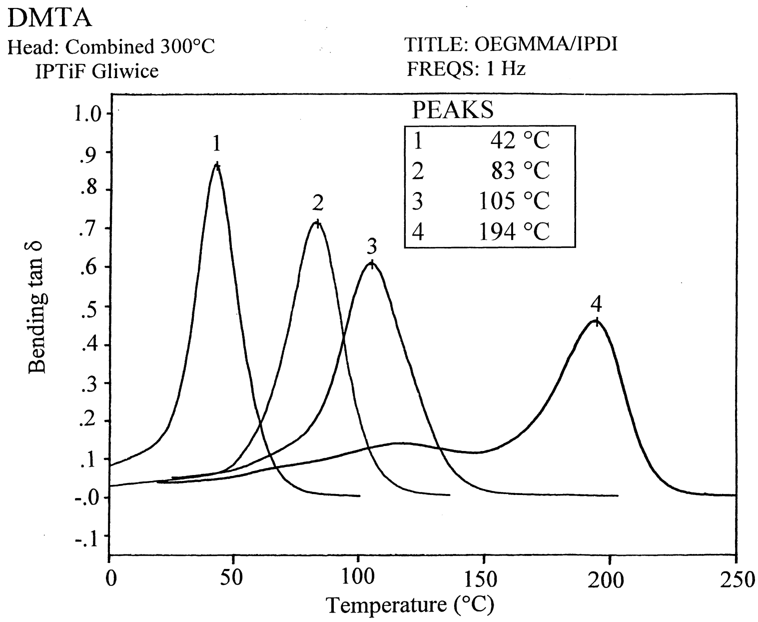

Fig. 2. DMTA runs for the polymers of: (1) TTEGMMA/IPDI; (2) TEGMMA/IPDI; (3) DEGMMA/IPDI; and (4) HEMA/IPDI.

(q), we employed the well-known definition of q formulated for "vinyl–divinyl" copolymerisation [8]:

$$q = \frac{2x_2}{m_1 + m_2 + 2x_2} \tag{2}$$

where x_2 is the number of moles of doubly reacted difunctional monomer; m_2 the number of moles of difunctional monomer in which one double bond has reacted; m_1 the number of moles of monofunctional monomer, which has reacted.

For polymerisation of dimethacrylates $m_1 = 0$, then

$$q = \frac{2x_2}{m_2 + 2x_2} \tag{3}$$

If each monomer molecule reacts with at least one double bond, the conversion can be expressed as:

$$\alpha = \frac{2x_2 + m_2}{2(x_2 + m_2)} \tag{4}$$

Combining Eqs. (3) and (4) we obtain:

$$\alpha = \frac{x_2}{2(x_2 + m_2)} + \frac{1}{2} = \frac{1}{2}\left(\frac{x_2}{x_2 + m_2} + 1\right)$$

$$2\alpha - 1 = \frac{x_2}{x_2 + m_2} \Rightarrow \frac{1}{2\alpha - 1} = \frac{x_2 + m_2}{x_2}$$

$$= \frac{2x_2 + m_2 + m_2}{2x_2} = \frac{2x_2 + m_2}{2x_2} + \frac{m_2}{2x_2}$$

$$\frac{1}{q} = \frac{2x_2 + m_2}{2x_2} = 1 + \frac{m_2}{2x_2} \Rightarrow \frac{m_2}{2x_2} = \frac{1}{q} - 1$$

$$\frac{1}{2\alpha - 1} = \frac{1}{q} + \frac{1}{q} - 1 \tag{5}$$

Finally, by solving Eq. (5), the crosslink density can be related to conversion by a simple equation:

$$q = \frac{2\alpha - 1}{\alpha} \tag{6}$$

From Eqs. (1) and (6) one can predict that when 50% of the double bonds have reacted ($\alpha = 1/2$), the crosslink density equals to 0, whereas the network parameter approaches infinity. A hypothetical polymer corresponding to such a situation in the simplest, extreme case could consist of comb-like macromolecules, where the chains would be formed by polymerisation of one of the double bonds of the dimethacrylates, while unreacted ones would form pendant groups. In the second extreme case conversion is full ($\alpha = 1$), thus $q = 1$ and $M_c = MW$. Two hypothetical systems might be considered here, a linear ladder-type polymer and a dense three-dimensional network. In both cases each repeating unit would correspond to one branch point whereas the network parameter would be related just to the crosslinks derived from single dimethacrylate molecules.

If less than 50% of C=C bonds was converted ($\alpha < 1/2$), the value of q would be negative. However, this would require the presence of a totally unreacted monomer in the system, which was excluded in the assumptions above. In real systems, i.e. in chemically or lightly cured dental restorative materials, the conversion of double bonds ranges from 55 to 75% [3]. This situation corresponds to q ranging from 0.182 to 0.667 and M_c from 5.5 to 1.5 MW, respectively. Assuming some intermediate, arbitrary value of $\alpha = 2/3$, we obtain $q = 1/2$ and $M_c = 2\,MW$. This implies that the network parameter in dental poly(dimethacrylate)s should be approximately twice as large as the molecular weight of the monomer.

It seems clear that the system cannot be considered in

Table 1
Glass transition temperature values measured by DMTA for the polymers of dicarbamates investigated

OEGMMA	T_g (°C) for the polymerised dicarbamate		
	HMDI	TMDI	IPDI
$n = 1$, HEMA	139	148	194
$n = 2$, DEGMMA	67	62	105
$n = 3$, TEGMMA	33	4	83
$n = 4$, TTEGMMA	−10	20	42

terms of Flory's representation of an ideal network, according to which a crosslink formed by difunctional molecule is depicted as a point, a volumeless, tetrafunctional species with respect to the rest of the chain [9]. Since molecular weights of dental dimethacrylates approach a few hundreds, and crosslinking densities are rather high; we should consider the crosslinks to be an important constituent of the structure of such a network, forming two trifunctional branch points between neighbouring primary chains.

4. Results

Polymers of the model OEGMMA/IPDI series were examined by DMTA to find some experimental evidence for the considerations presented above. The temperature dependence of the loss tangent presented in the Fig. 2 yielded values of the glass transition temperature. The latter are compared in the Table 1 with those determined previously for the polymers of the OEGMMA/HMDI and OEGMMA/TMDI series [6,10]. A distinct dependence of T_g on both molecular weight and chemical structure of the dimethacrylates is seen from the collected data: T_g increases in all the series as molecular weight decreases, i.e. the networks become more rigid, assuming crosslink densities to be similar. Structural effects appear when the OEGMMA/TMDI and OEGMMA/IPDI series are compared. The T_g values differ distinctly between these series despite the fact that polymers have comparable molecular weights (see Tables 1 and 2).

Determination of T_g is the most frequently used application of DMTA. However, this technique is also capable of generating other valuable information on the structure of polymeric systems, including crosslinked ones. Thus, from the measurements of storage modulus (E') at the temperatures above T_g (in the rubbery plateau region) it is possible to evaluate the network parameter M_c from the following relationship [2].

$$M_c = \frac{3RT\rho}{E'} \tag{7}$$

where ρ is the density (g/cm^3), T is the temperature (K), E' is the storage modulus (MPa) and R is the universal gas constant.

The values of M_c for the three series of polymers investigated have been calculated from the values of E' measured by DMTA and the experimental densities. The results are collected in Table 2 along with the molecular weights of the corresponding dimethacrylate monomers, while Fig. 3 presents the ratios of the former to the latter. The values of M_c/MW ratio can be understood as the number-average degrees of polymerisation between two crosslinks.

A striking result is that for all the OEGMMA/IPDI series and for the first two members of the OEGMMA/HMDI series, the calculated values of M_c are lower than the corresponding MWs. Presumably, DMTA measurements are sensitive to the presence of some additional branch points resulting from the existence of any non-covalent bonds between primary chains, crosslinks and (in the systems investigated) also pendant groups. Urethane bonds are known to be susceptible to forming strong intermolecular hydrogen bonds with ether, ester and other urethane groups present in the system [11–13], and which could be responsible for the above finding, particularly because the concentration of such a species in the polymers investigated is rather high. For the polymers of the OEGMMA/IPDI series the possibility that DMTA recognises tertiary carbons of aliphatic ring as additional branch points cannot be excluded.

The above explanation is supported by the ^{1}H NMR

Table 2
Network parameter values evaluated by DMTA for aliphatic poly(urethane dimethacrylate)s and molecular weights of the corresponding monomers

Sample	Density (g/cm^3)	T (K)	E' (MPa)	M_c (g/mol)	*MW* (g/mol)
HEMA/HMDI	1.28	473	108	140	429
DEGMMA/HMDI	1.243	407	59	214	517
TEGMMA/HMDI	1.234	338	9	1156	605
TTEGMMA/HMDI	1.229	303	9	1032	693
HEMA/TMDI	1.236	463	26	549	471
DEGMMA/TMDI	1.231	378	19	611	559
TEGMMA/TMDI	1.212	323	5	1953	647
TTEGMMA/TMDI	1.321	333	14	784	735
HEMA/IPDI	1.39	508	62	284	483
DEGMMA/IPDI	1.20	433	41	316	571
TEGMMA/IPDI	1.27	403	42	304	659
TTEGMMA/IPDI	1.23	353	22	492	747

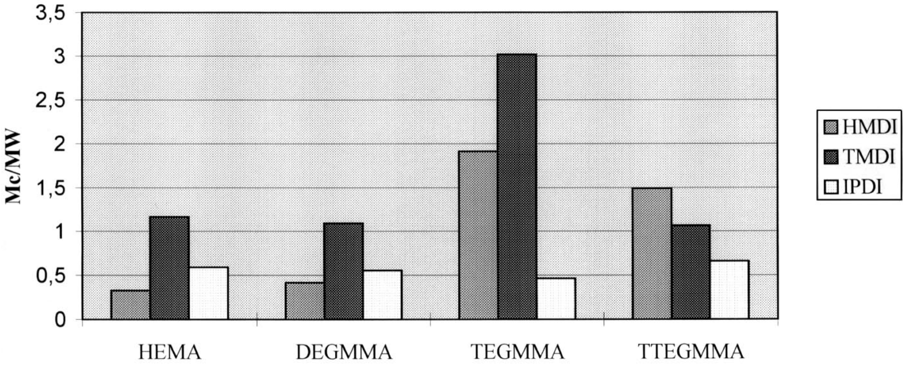

Fig. 3. Structural dependence of the ratio of the network parameter to the molecular weight of monomer (M_c/MW) for the series of poly(urethane dimethacrylate)s.

experiments on the monomers in solution. We found that, on dilution, the signals of NH protons experience strong upfield shifts of up to 0.5 ppm when changing the concentration from about 30 to 0.12 wt% (Fig. 4). This effect is too large to be explained by interactions with solvent only, particularly because the chemical shifts of other protons practically do not change. Simultaneously, spin-spin coupling with neighbouring α-protons is visible, thus excluding intermolecular exchange phenomena. Most probably the effect observed is due to the existence of molecular associations in solution, resulting from formation of intermolecular non-covalent interactions, e.g. hydrogen bonds, involving urethane groups. We suspect analogous interactions occur between the pendant side chains and the crosslinks in the poly(dimethacrylate)s investigated, which would underestimate the values of the network parameter measured.

Presumably, it is possible to find some deeper structural relationship based on the results obtained. This would require, however, a precise knowledge of the conversion of double bonds in each individual polymer investigated. Determination of the lengths of primary chains seems to be essential as well, and both these are rather difficult tasks. Work directed to achieve these objectives is underway.

5. Conclusions

Dynamic mechanical thermal analysis appeared to be capable of determining network parameters for a series of aliphatic poly(urethane-dimethacrylate)s.

The resulting values of M_c were found to be lower than those predicted on the basis of theoretical considerations.

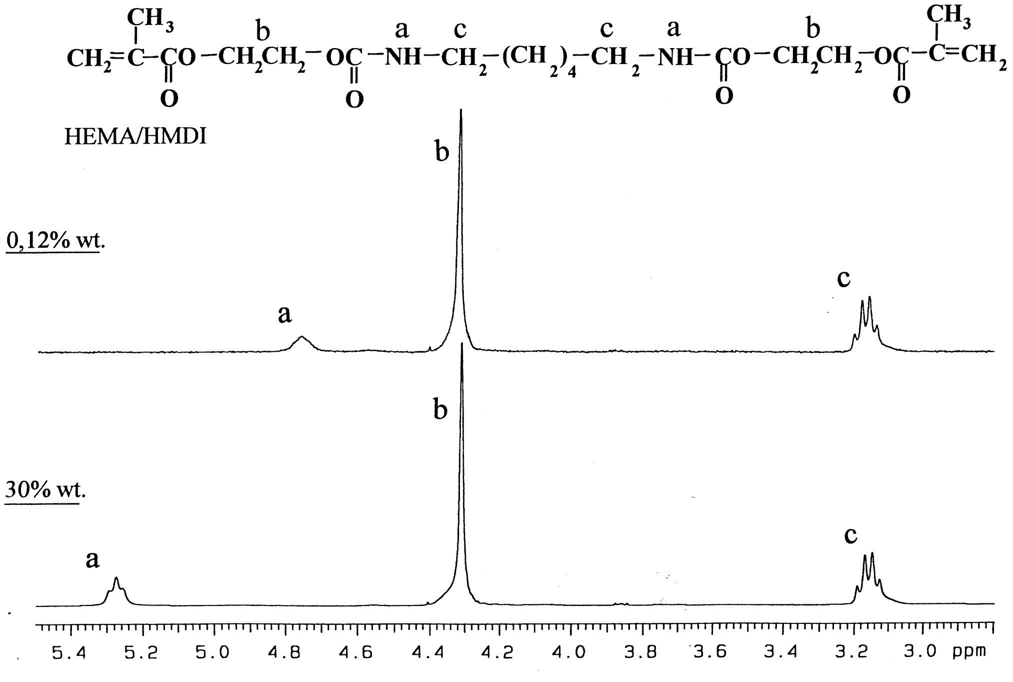

Fig. 4. Fragments of 1H NMR spectra of concentrated (lower trace) and diluted (upper trace) solutions of HEMA/IPDI monomer.

This observation can be explained by the existence of additional junction points in the networks, resulting from intermolecular hydrogen bonds involving urethane linkages.

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