

Quantitative Determination of Degree of Conversion in Photocured Poly(urethane-dimethacrylate)s by Fourier Transform Infrared Spectroscopy

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ABSTRACT: In this work, infrared spectroscopy was used to characterize the degree of double bonds conversion (DC) in six series of poly(urethane-dimethacrylate)s, derived from dicarbamates of oligoethylene glycols monomethacrylates and aliphatic, cycloaliphatic and aromatic diisocyanates. To evaluate the degree of conversion in polymers devoid of aromatic moieties, two methods of calculation have been proposed: internal band ratio method, with carbonyl stretching vibrations as a standard, and a method involving the direct observation of the decrease in the intensity of C=C stretching band. The validity of these methods has been checked on polymers with aromatic structures, by comparing the results with those obtained

by the internal band ratio method applying an aromatic band as a reference. A good correlation between the degree of conversion from two internal standard methods, using aromatic band and carbonyl band as references, was obtained. It was shown that the degree of conversion increases as the number of oxyethylene units increases. Polymerization of monomers with aliphatic cores resulted in higher DC values, while those with cycloaliphatic and aromatic cores—resulted in lower DC values. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1604–1611, 2012

Key words: dimethacrylates; infrared spectroscopy; degree of conversion; polymer networks

INTRODUCTION

The dimethacrylate-based polymeric networks have become a very attractive research area simultaneously combining fundamental and applied topics of great interest. They are used as abrasion-resistant coatings,^{1–3} components in optical telecommunication^{4,5} and dental restorative materials.^{6–10}

A great problem with the application of dimethacrylate-based polymers is the depth of the polymerization and how to appropriately measure it. The polymerization of multifunctional methacrylates generally exhibits certain complex features such as autoacceleration, autodeceleration, steric isolation, and vitrification. All the above factors lead to a decrease in the degree of double bonds conversion (DC), which is significantly less than 100%, despite the presence of trapped radicals and double bonds, which did not react. The unreacted double bonds may be present either as pendant groups in the network or in free monomer molecules, which may even leach from the polymerized material. Only

very flexible monomers, in which the reactive methacrylate groups are relatively far apart, can be completely reacted. Thus, the DC generally depends on the chemical structure of the monomer.^{5,7,11–13}

The DC is a major factor influencing the physical properties of resulted cross-linked polymers. The higher the conversion of double bonds, the higher the mechanical strength, modulus and hardness.^{2,3,7–10,14,15}

Since the structure of polymer network formed, characterized by the DC, has considerable influence on the final mechanical properties, knowledge of the DC is essential.

Fourier transform infrared (FTIR) spectroscopy is an established analytical technique that has been adopted as a standard, convenient, and reliable method for assessing the DC in multi(meth)acrylate systems.^{2–4,7,10,12,14–24}

To determine the DC by vibrational spectroscopy, the disappearance of signals generated by vibrations of double vinyl bonds are monitored. The content of methacrylate groups remaining in the sample after irradiation can be estimated by the intensities of the peaks, either at 1637 cm⁻¹ referring to the C=C stretching or at 816 cm⁻¹ referring to the C=C twisting. More often the 1637 cm⁻¹ absorption is chosen, because it is stronger than that at 816 cm⁻¹ and provides less experimental deviation.^{3,7,9,10,12,14–20,24}

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In the determination of the DC, the relative band ratio method is widely used. In this method, the intensity decrease of the vinyl bond vibrations, resulting from polymerization, is determined in relation to the vibrations which do not take part directly in the polymerization reaction (internal standard). An assumption for the application of this method is that the relative absorptivity of the reference vibrations in the monomer and in the polymer are equal.⁴

The aromatic C=C stretching vibration at 1609 cm^{-1} is used as an established internal standard.^{3,4,7,10,14-18} In some studies, when resins do not contain aromatic rings, C=O stretching vibration at 1720 cm^{-1} is used as a standard.^{4,17,19,22-24} The results of that method may be inaccurate and many scientists negate C=O band usefulness as a standard.^{3,7,20}

It has been reported that the position and the intensity of the sharp well-defined peak, assigned to the carbonyl stretching vibration, change during polymerization. In the uncured state the carbonyl group is conjugated with the C=C bond and on curing this conjugation is lost. The bond becomes stronger in the cured state due to the fact that the electrons are no longer delocalized and a significant loss of intensity of this peak has been observed. This effect can also be influenced by a decreased strength of intra- and intermolecular hydrogen bonds in a polymer.^{7,14,25}

For systems having no aromatic rings, a method of the continuous measurement of C=C absorbance during the irradiation, known as real time infrared spectroscopy (RT-FTIR), is often used. This method does not require a standard and enables the calculation of conversion at any time of polymerization directly, by dividing C=C absorbance, measured at time t (in the polymer), by its initial absorbance (in the monomer).^{7,12,20,21}

The aim of this work was to develop a methodology whereby the dimethacrylate monomers conversion, which contain no aromatic group, can be elaborated using infrared spectroscopy and then to correlate their chemical structure with the DC. These are twenty four urethane-dimethacrylates (UDMA) obtained from oligoethylene glycols monomethacrylates (OEGMMA), having from 1 to 4 oxyethylene units, and six diisocyanates (DI): aliphatic—HMDI and TMDI, cycloaliphatic—IPDI and CHMDI, aromatic—TDI and MDI (Fig. 1). Only two of them: HEMA/HMDI and HEMA/TMDI are used in practice, the remaining monomers are new and of potential application.^{7,8} The quantitative determination of saturation in polymer networks obtained from light-induced homopolymerization of these monomers was carried out by FTIR spectroscopy. The only two homologue series of polymers among those examined contain aromatic moieties: poly(OEGMMA/

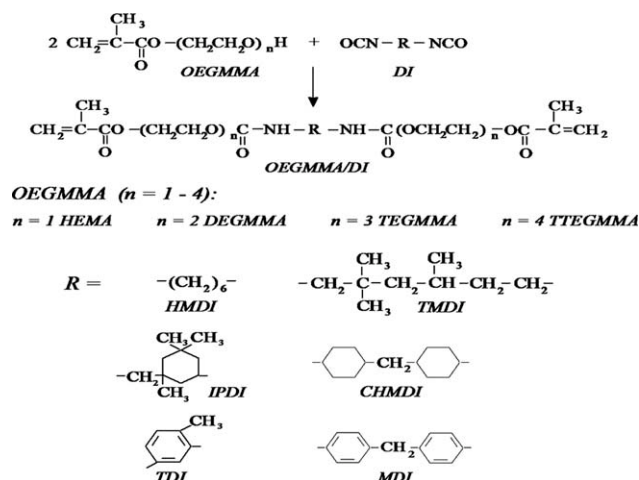


Figure 1 Structure of UDMA monomers.

MDI) and poly(OEGMMA/TDI), and only for those is it possible to apply the well established method of calculation of the DC, by using the band of aromatic vibrations as a standard. The DC for remaining polymers has to be calculated in a different way. For that purpose, the validity of the DC calculation with the use of C=O band as a standard and direct measurements of intensity of methacrylate C=C bands in monomers and polymers has been checked.

By comparing the DC in poly(OEGMMA/TDI) and poly(OEGMMA/MDI) calculated in the following three ways: two relative band ratio methods (with C=C aromatic band and C=O band used as standards) and the direct method (without a standard), the methodology for calculating the DC was elaborated for the whole group of UDMA polymers, including those without aromatic groups: poly(OEGMMA/HMDI), poly(OEGMMA/TMDI), poly(OEGMMA/IPDI), and poly(OEGMMA/CHMDI).

Possessing knowledge of the DC is essential in understanding structure–property relationships of dimethacrylate polymer networks and can help in controlling, modifying and improving the final properties of cross-linked polymeric materials originating from this type of monomers.

EXPERIMENTAL

Materials

Urethane-dimethacrylate (UDMA) monomers were synthesized from OEGMMA and DI according to the procedure previously reported.^{26,27} 2-Hydroxyethyl methacrylate (HEMA; Sigma), hexamethylene-1,6-diisocyanate (HMDI; Fluka), 2,2,4^{2,4,4}-trimethylhexyl-1,6-diisocyanate (TMDI; Aldrich), isophorone diisocyanate (IPDI; Aldrich), 4,4'-methylenebis(cyclohexyl isocyanate) (CHMDI; Aldrich), 2,4-toluene diisocyanate (TDI; Aldrich) and 4,4'-methylenebis(phenyl isocyanate) (MDI; Aldrich) were used as received. Monomethacrylates: DEGMMA, TEGMMA and TTEGMMA

TABLE I
Thermal Properties of UDMA Monomers and Temperatures of Their Polymerization

OEGMMA	$T_m/T_p/T_o$ (°C)					
	HMDI	TMDI	IPDI	CHMDI	TDI	MDI
$n = 1$ HEMA	77/91/155	RT _p	RT _p	108/125/195	98/114/181	89/103/161
$n = 2$ DEGMMA	RT _p	RT _p	RT _p	RT _p	RT _p	RT _p
$n = 3$ TEGMMA	RT _p	RT _p	RT _p	RT _p	RT _p	RT _p
$n = 4$ TTEGMMA	RT _p	RT _p	RT _p	RT _p	RT _p	RT _p

T_m , melting temperature of the monomer; T_p , temperature at which the photopolymerization was carried out; T_o , onset of the temperature of thermal polymerization; RT_p, room temperature, at which liquid monomers were photopolymerized.

were obtained from methyl methacrylate (MMA; Acros) and corresponding glycols: diethylene (DEG; Acros), triethylene (TEG; Acros), and tetraethylene (TTEG; Acros) ones according to the procedure described previously.^{26,27} The purity of all the monomers was checked by means of ¹H NMR analysis (UNITY/INOVA, VARIAN, 300 MHz) in CDCl₃, using tetramethyl silane as an internal standard.

Polymerization

To photopolymerize the samples, 0.4 wt % of camphorquinone (CQ; Aldrich) used as photosensitizer and 1 wt % of *N,N*-dimethylaminoethyl methacrylate (DMAEMA; Aldrich) used as reducing agent, were added to each sample.

Photopolymerization was initiated with a mercury lamp (FAMED-1, model L-6/58, Poland, power 375 W), set at a distance of 15 cm and irradiated for 5 min. This lamp emitted radiation in the 420–500 nm range, where CQ absorbs ($\lambda_{max} = 470$ nm).⁷ The monomer samples were covered with PET film to reduce oxygen inhibition effects.

Majority of all UDMA monomers are viscous liquids, except for HEMA/HMDI, HEMA/CHMDI, HEMA/TDI, and HEMA/MDI, which are crystalline solids (Table I). Liquid monomers were room temperature photopolymerized (RT_p). Solid monomers were photopolymerized in the molten state. The temperature of curing was chosen on the basis of DSC measurements.

Determination of the temperature of photopolymerization (T_p) of solid UDMA monomers by DSC

The calorimetric measurements were carried out on a Mettler Toledo differential scanning calorimeter (DSC 822°). Samples of ~ 2 mg each were heated from 20 to 250°C with a heating rate 10 K/min.

The temperature of photopolymerization of solid monomers have been selected at 10 K above endset of the melting process, which was the safe temperature at which the thermal polymerization did not take place (Fig. 2, Table I).

Degree of conversion (DC)

The DC in UDMA polymers was determined by using FTIR spectrophotometer (Bio-Rad FTS 175C). The spectra of the monomers and their polymers were recorded with 128 scans at resolution of 1 cm⁻¹. The absorption intensity of selected peaks was measured after the baseline correction in the 1800–1500 cm⁻¹ region.^{14,16}

The FTIR measurements were carried out in two ways, depending on the physical state of the monomer at room temperature.

Measurement of liquid monomers conversion

A very thin film of mixture of each liquid monomer (Table I) containing initiating system was formed onto potassium bromide pellet and FTIR spectrum has been recorded at zero time (t_0). Then the sample was irradiated for 5 min (t_t). The spectra of the polymers were recorded immediately after the end of irradiation.

Measurement of solid monomers conversion

The mixtures of solid monomers (Table I) with initiating system were polymerized for 5 min at elevated temperatures (selected for each solid monomer

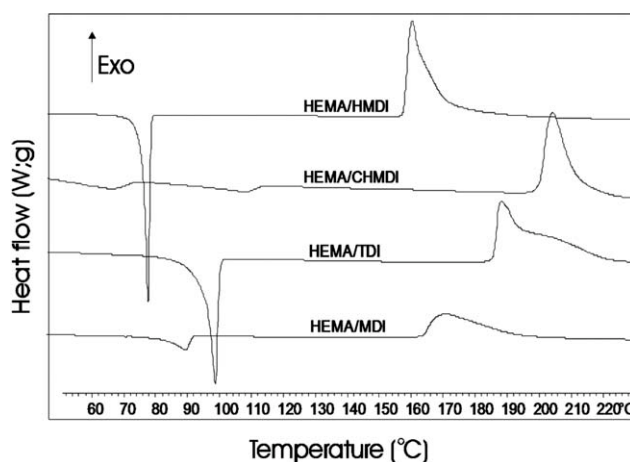


Figure 2 DSC curves of UDMA monomers being solid at room temperature.

in DSC measurements) in a form of very thin film formed on a glass plate. The cured samples were pulverized into fine powder with a planetary ball mill (Pulverisette, Fritsch GmbH) and next sifted to a particle diameter less than 24 μm . The samples of those polymers were admixed with potassium bromide and examined as pellets.

Calculations of the DC

The DC in UDMA polymers was calculated according to the following ways:

- In relation to the peak at 1598 cm^{-1} assigned to aromatic stretching vibrations, in the case of monomers of series having aromatic moieties (OEGMMA/TDI and OEGMMA/MDI):

$$DC_{Ar} = 1 - [(A_{C=C}/A_{Ar})_{\text{polymer}} / (A_{C=C}/A_{Ar})_{\text{monomer}}] \quad (1)$$

where, $A_{C=C}$ is the absorption of the peak at 1637 cm^{-1} and A_{Ar} is the absorption of the peak at 1598 cm^{-1} .

- In relation to the peak at 1718 cm^{-1} assigned to the carbonyl stretching vibration as follows:

$$DC_{C=O} = 1 - [(A_{C=C}/A_{C=O})_{\text{polymer}} / (A_{C=C}/A_{C=O})_{\text{monomer}}] \quad (2)$$

where, $A_{C=C}$ is the absorption of the peak at 1637 cm^{-1} and $A_{C=O}$ is the absorption of the peak at 1718 cm^{-1} . This method was applied for photopolymerization of all, liquid and solid, monomers.

- Directly, from the decrease of absorption band referring to the $C=C$ stretching vibrations at 1637 cm^{-1} on the FTIR spectra as follows:

$$DC_{C=C} = 1 - (A_{C=C(t)} / (A_{C=C(0)})) \quad (3)$$

where, $A_{C=C(0)}$ is the absorption of the peak at 1637 cm^{-1} at the start and $A_{C=C(t)}$ the absorption at the end of photopolymerization (after 5 min). This method was applied only in the case of photopolymerization of liquid monomers.

RESULTS AND DISCUSSION

Twenty four UDMA monomers of various structures (from very elastic to very rigid; Fig. 1) have been used to synthesize UDMA networks. The system has been thought to be a model one when investigating the influence of the chemical structure of dimethacrylate monomer on the DC in a polymer. Two structural parameters of UDMA were changed: the length of oligoxyethylene chain, having from one to

four oxyethylene units, and the chemical character of the core, derived from DI, being: aliphatic (HMMDI, TMMDI), cycloaliphatic (IPDI, CHMDI), or aromatic ones (TDI, MDI). The monomers were activated for visible light photopolymerization by the addition of CQ 0.4 wt % and DMAEMA 1 wt %.

Depending on the physical state of the monomer the polymerization was carried out in two ways. Photopolymerizations of all the liquid monomers, being in the majority, were performed directly on the KBr pellet, as a very thin film, at room temperature, under identical conditions to obtain comparable results. Since the monomers: HEMA/HMMDI, HEMA/CHMDI, HEMA/TDI, and HEMA/MDI are solid, their photopolymerization required transformation to liquid state before the reaction. They were polymerized on a glass plate, as a very thin film at elevated temperatures. The temperature of photopolymerization (T_p) for those monomers has been estimated by use of DSC experiments and was selected 10 K above endset temperature of melting (T_m), which was lower than the onset temperature of thermal polymerization (T_o) (Table I). The monomers: HEMA/HMMDI, HEMA/CHMDI, HEMA/TDI, and HEMA/MDI were photopolymerized at the following temperatures, respectively: 91°C , 125°C , 114°C , and 103°C .

TABLE II
The Degree of Conversion (DC) in Light-Cured UDMA Polymers Calculated According to Discussed Methods

Polymer	DC_{Ar} (%)	$DC_{C=O}$ (%)	$DC_{C=C}$ (%)
HEMA/HMMDI	–	67	^a
DEGMMA/HMMDI	–	83	88
TEGMMA/HMMDI	–	93	97
TTEGMMA/HMMDI	–	92	91
HEMA/TMDI	–	48	76
DEGMMA/TMDI	–	63	79
TEGMMA/TMDI	–	90	82
TTEGMMA/TMDI	–	88	89
HEMA/CHMDI	–	27	^a
DEGMMA/CHMDI	–	66	69
TEGMMA/CHMDI	–	79	75
TTEGMMA/CHMDI	–	81	87
HEMA/IPDI	–	23	51
DEGMMA/IPDI	–	41	70
TEGMMA/IPDI	–	86	91
TTEGMMA/IPDI	–	85	80
HEMA/MDI	47	23	^a
DEGMMA/MDI	56	47	57
TEGMMA/MDI	85	84	79
TTEGMMA/MDI	89	89	87
HEMA/TDI	42	31	^a
DEGMMA/TDI	71	67	68
TEGMMA/TDI	72	64	58
TTEGMMA/TDI	75	69	84

^a The direct measure of intensity of $C=C$ methacrylate band in monomer and polymer have not been done because of solid state of the monomer at room temperature.

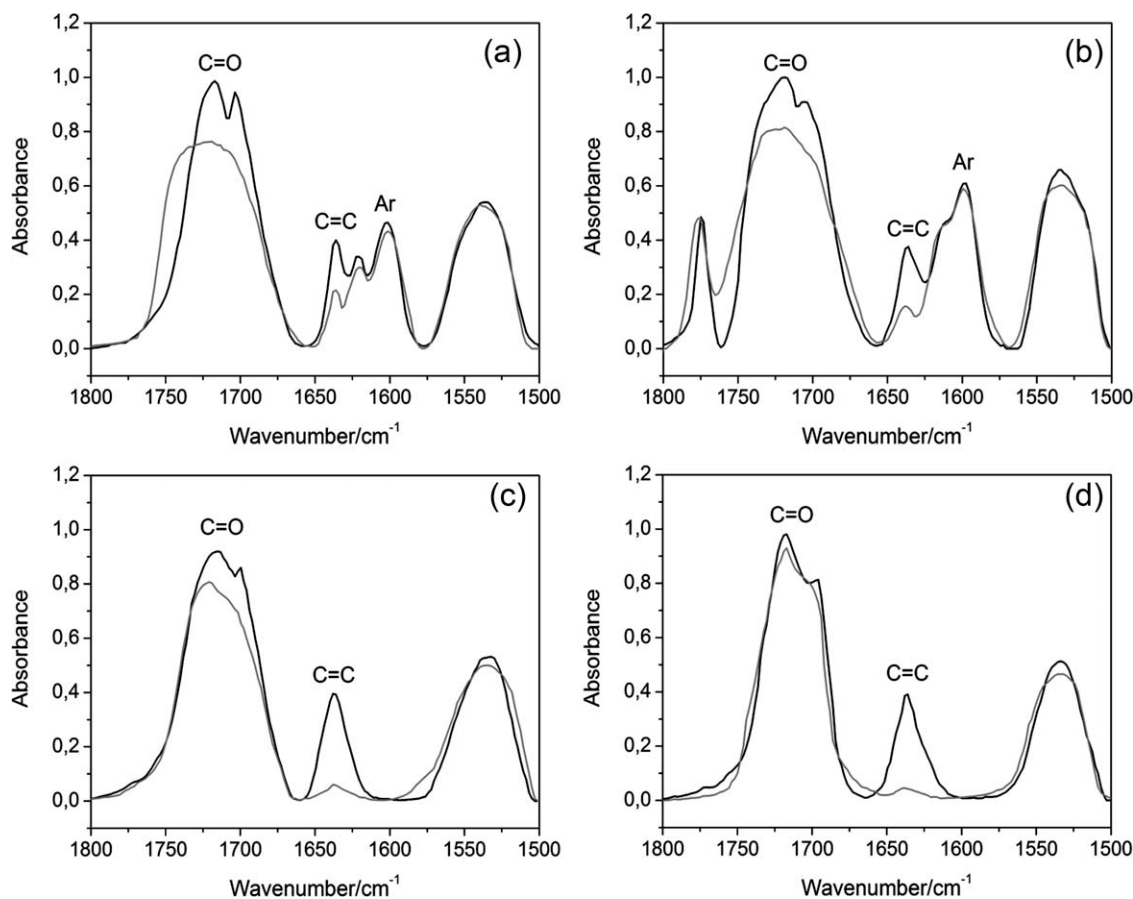


Figure 3 The exemplary FTIR spectra of: HEMA/TDI (a), DEGMMA/MDI (b), TEGMMA/IPDI (c), and TTEGMMA/HMDI (d) (black—the monomer, gray—the polymer).

When IR spectroscopy is applied to investigate the DC in poly(dimethacrylate)s, the internal band ratio method with stretching vibrations of aromatic ring as a reference is the most frequently used. Only two homologue series of monomers among the examined ones contain aromatic moieties: OEGMMA/MDI and OEGMMA/TDI, and only for those was it possible to apply this method. The control of the DC in the remaining polymers was a more difficult task, especially due to the lack of an unquestionable FTIR method of the DC determination in poly(dimethacrylate)s devoid of aromatic moieties. To evaluate the DC in polymers of all six homologue series of UDMA, two other methods of calculations have been proposed: internal band ratio method with carbonyl stretching vibrations as a standard and the method involving the direct observation of the decrease in the intensity of C=C stretching band. Since these methods have as many followers^{4,17,19,22,24} as opponents,^{3,7,20} their validity has been checked on OEGMMA/MDI and OEGMMA/TDI series, by comparing the results with those obtained from internal band ratio method using aromatic band as a reference, being the widely accepted one (Table II).^{3,4,7,10,14–16,18}

In FTIR spectra of UDMA monomers usually two C=O bands can be distinguished (Fig. 3). When C=O band was used as a standard, the DC was calculated in respect to the intensity of C=O band at 1718 cm^{-1} , as more reliable than the one at 1699 cm^{-1} . The band at the lower wavenumber is identified for the carbonyl group affected by hydrogen bonds, and the other one as the “free” carbonyl group.^{14,20} Presence of the doublet of the C=O stretching vibrations can be also explained by the complex structure of UDMA monomers, where the carbonyl group is part of both ester (—COO—) and urethane (—NHCOO—) linkages.

The precision of the internal standard method using C=O band as a reference was tested by comparing the DC obtained in this way with the DC determined by the method using aromatic band as a reference (Fig. 4). In Figure 4(a) results only for liquid monomers are compared. The results for all monomers of the series OEGMMA/MDI and OEGMMA/TDI, including HEMA/MDI and HEMA/TDI, are shown in Figure 4(b). In both cases, good linear relationships were found, respectively: $R^2 = 0.988$ and $R^2 = 0.966$. However, it has been noticed, that the DC values from the method where

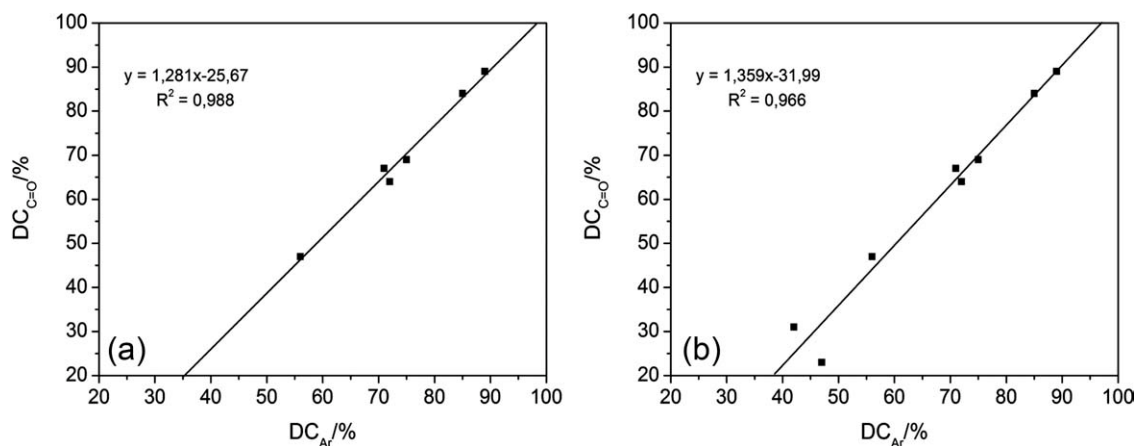


Figure 4 A comparison of the degree of conversion obtained from the internal standard method using the aromatic band (DC_{Ar}) with the degree of conversion from the internal standard method using the carbonyl band ($DC_{C=O}$) in UDMA polymers based on MDI and TDI: (a) except and (b) including poly(HEMA/MDI) and poly(HEMA/TDI).

carbonyl reference band is used are lower than the DC values from the method involving aromatic reference band (Table II). This observation is in agreement with the statement that C=O band becomes less intense in the course of polymerization.²⁵ The offset of the DC depends on the structure of the polymerizing monomer. For short and stiff HEMA/MDI and HEMA/TDI molecules, the DC differ significantly, respectively: 51 and 26%. The strength of hydrogen bonds, which increases with the decrease of the length of oligooxyethylene chains in UDMA structures,²⁷ can play an additional role in this case. The intensity of the carbonyl band in the monomer spectrum can be significantly higher in respect to the polymer spectrum, which results in a smaller DC value. The DC of monomers of symmetrical, elastic molecules with longer oligooxyethylene chains (TEGMMA/MDI and TTEGMMA/MDI) are almost the same in both methods. On the above, the application of the C=O band as a reference in the determination of the DC may be regarded for calculations to get quantitative conversion data in the series of UDMA polymers.

The method based on the direct measurement of decreasing intensity of methacrylate C=C band was checked as well. This method can not be used for systems based on: HEMA/HMDI, HEMA/CHMDI, HEMA/TDI, and HEMA/MDI, obtained in indirect polymerization. In Figure 5, the relationship between the DC calculated by the methods using aromatic band as a standard and direct measurement of intensity of C=C band in monomer and polymer is shown. A poor linear relationship ($R^2 = 0.667$) makes this methodology unacceptable for estimation of the DC in UDMA polymers.

In Table II, the DC values in all investigated polymers calculated by all methods discussed are summarized.

For further considerations of the monomer structure/the DC relationship, the internal standard method involving carbonyl band as a reference was chosen. Since, the DC values determined by this method appeared to be lower than in reality, the linear regression equation $DC_{C=O} = f(DC_{Ar})$ was used to recalculate the obtained values of the $DC_{C=O}$ (Fig. 6).

As shown in Figure 6, when comparing the DC in polymers of all homologous series, the dependence on chemical structure of monomers is observed. The DC increases with the length of the oligooxyethylene chain, but for the monomers with the longest molecules it drops slightly. The influence of the chemical

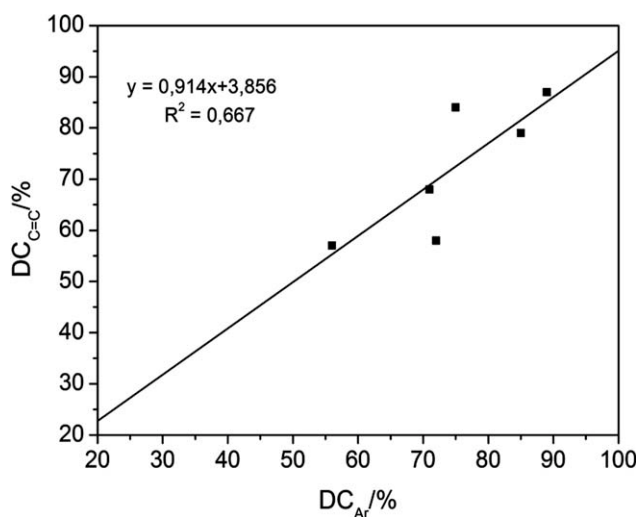


Figure 5 The degree of conversion in UDMA polymers based on MDI and TDI, calculated according to the internal standard method using the aromatic band (DC_{Ar}) versus the degree of conversion calculated according to the direct method of observation C=C band ($DC_{C=C}$).

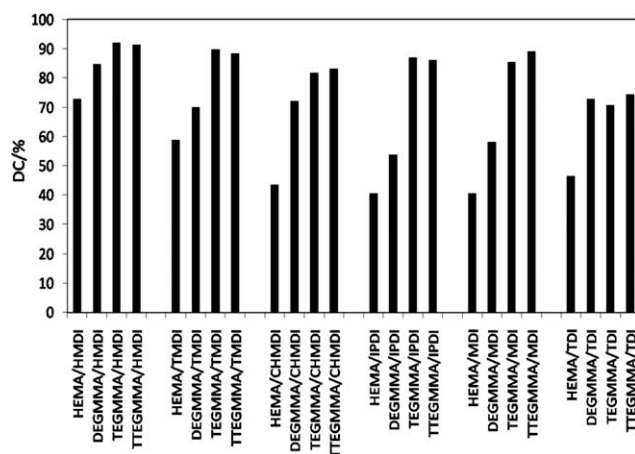


Figure 6 The degree of conversion (DC) in all UDMA polymers predicted by using the linear regression analysis.

character of the core in repeating units is also seen. The DC in poly(UDMA)s with cycloaliphatic and aromatic moieties in their structures are lower in comparison to the fully aliphatic polymers.

The stiff cycloaliphatic or aromatic cores as well as strong hydrogen bonding between short UDMA structures (HEMA/DI) can cause a decreased mobility of monomer molecules during polymerization, resulting in lower DC than expected. The reason for this result can also be the significant loss of the absorption intensity of the C=O band due to the decreased strength of hydrogen bonds in polymers.

However, the —NH— groups, present in UDMA monomers can cause chain transfer reactions which increase the mobility of radical sites on the network and thereby offer an alternative path of continued polymerization. These chain-transfer reactions may be responsible for the high polymerization reactivity of UDMA monomers, what leads to higher DC, for longer, more elastic molecules (based on TEGMMA and TTEGMMA).

CONCLUSIONS

The DC in UDMA polymers of different structure was studied by FTIR. Two internal standard methods and the method of direct observation of the decrease of C=C band has been proposed for validating the DC in poly(urethane-dimethacrylate)s.

The results showed that the method using carbonyl band as a standard may be applied for calculation of the DC in UDMA polymers, but under several conditions. The length and the elasticity of the monomer molecule determine the accuracy of the results. For long and elastic monomer molecules the DC values are reliable. The greater their stiffness the greater the experimental deviation produced. However, the deviation can be predictable when constructing the well-

defined model system of polymerizing monomers. This method yields lower values of the DC when compared with the results from the method using aromatic band as a standard, but a good linear relationship between them is obtained.

The results from the direct observation of the decrease in the intensity of C=C stretching band show a poor relationship with others discussed in the work methods and make this method unacceptable for the DC calculations. This result suggests that in one work, for comparison purposes, one method of calculation should be chosen. It is not possible to apply different methods for each particular monomer.

The DC in UDMA polymers depends on the length of the oligoxyethylene chain and chemical character of the core in the repeating unit. After the initial growth of the DC with an increasing number of oxyethylene units, it drops slightly for the longest UDMA molecules. Replacing the aliphatic core by a cycloaliphatic or an aromatic core results in a decreasing DC.

The stiffness of HEMA-based monomer molecules resulting from the presence of cyclic (cycloaliphatic or aromatic) structures, short oxyethylene units and a higher concentration of hydrogen bonds, leads to lower DC values.

The great elasticity of longer UDMA monomer molecules (TEGMMA and TTEGMMA based) leads to higher DC values.

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