Determination of the Monomer Reactivity Ratios in Copolymerization of Two Distinct Dimethacrylates for Dental Use

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The copolymerization reaction between bisphenol A glycerolate dimethacrylate (BisGMA) and urethane dimethacrylate (UDMA) monomers was studied and the monomer reactivity ratios were determined on the base of the FTIR data obtained at different times of reaction. Both Fineman-Ross and copolymer composition equations were used. Also ProCop computation program was used in order to establish the values for the reactivity ratios.

Keywords: Dimethacrylates; Copolymerization; Monomer Reactivity Ratios; FTIR; ProCop

The group of methacrylate-based polymers is a common subject of interest both for researchers and industry. The dimethacrylate monomers exhibit good mechanical properties like moderately high Young modulus, strength and hardness so that they can be used for biomedical implants [1, 2], dental resins [3] and coatings [4].

The dimethacrylates BisGMA (bisphenol A glycerolate dimethacrylate) and UDMA (urethane dimethacrylate) are widely used as the base monomers in the formation of the polymeric matrices for dental composites. These two monomers are comparable in size but differ in their chemical structure which affects critical properties such as viscosity, diffusion coefficients, vinyl group conversion, shrinkage, water uptake and mechanical properties. A common feature of BisGMA and UDMA is their ability to form physical crosslinks via hydrogen bonding that can increase the basic strength and modulus of their dimethacrylate-based polymers which are mainly achieved by carbon-carbon covalent bonding, especially in the form of chemical crosslinks of the network structure [5].

The aim of our work was to follow the copolymerization process between UDMA and BisGMA through FTIR spectrometry and then to calculate the monomer reactivity ratios by different methods [6-9].

The monomer reactivity ratios are very important parameters which may offer information about relative reactivity of monomer pairs, elucidation of copolymer structure, copolymer composition and monomer sequence [10].

Experimental part

Materials

The dimethacrylate monomers used were bisphenol A glycerolate dimethacrylate (BisGMA) and urethane dimethacrylate (UDMA). These monomers were used as received without further purification. The free radical initiator was benzoyl peroxide (BP) that was recrystallized from methanol and dried in a dessicator under vacuum, at room temperature, for 1 day. The chemical structures of the raw materials are shown in figure 1.

Copolymerization

In order to estimate the dimethacrylates monomers reactivity ratios, different binary systems were prepared by mixing the UDMA and BisGMA monomers in different amounts: 90%w + 10%w (Substrate 1, $\mathbf{S_1}$), 80%w + 20%w (Substrate 2, $\mathbf{S_2}$), 70%w + 30%w (Substrate 3, $\mathbf{S_3}$). All the systems were initiated with 1% BP by heating at 80°C. Several samples were taken every 5 min up to 50 min. Each collected sample was cooled on ice for 10 min in order to stop the polymerization reaction. Further on the sample was introduced in 5 ml methanol, which is solvent for unreacted monomers and nonsolvent for the formed copolymer.

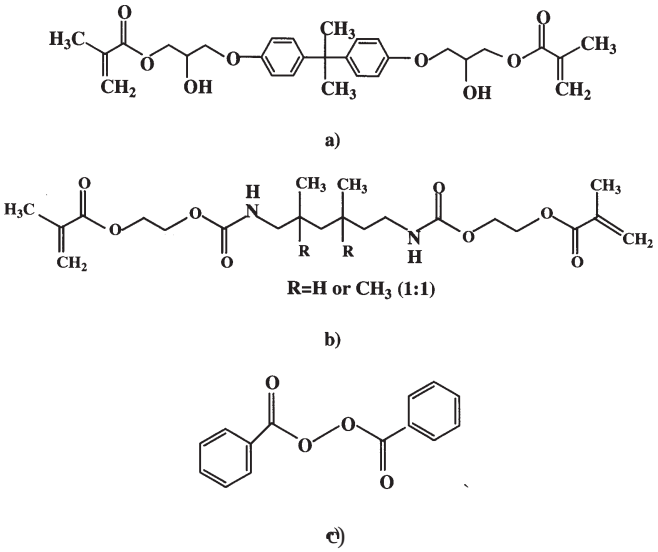


Fig. 1. The chemical structure of dimethacrylate monomers and free radical initiator: a) BisGMA; b) UDMA; c) BP

The obtained copolymer was filtered, dried by free evaporation (r.t., 3 days) and weighted. After the solid part (copolymer) was removed, the unreacted monomers remain in solution. From the filtered solution, three different samples were separated, for a good reproductibility, and FTIR spectra were registered.

Characterization technique

Absorbance FTIR spectra were recorded using a VERTEX 70 BRUCKER equipment. The spectra were collected over the 4000 to 400 cm^{-1} wavenumber range.

Calibration curve

A calibration curve is first required in order to establish the concentration of a compound from a mixture by IR

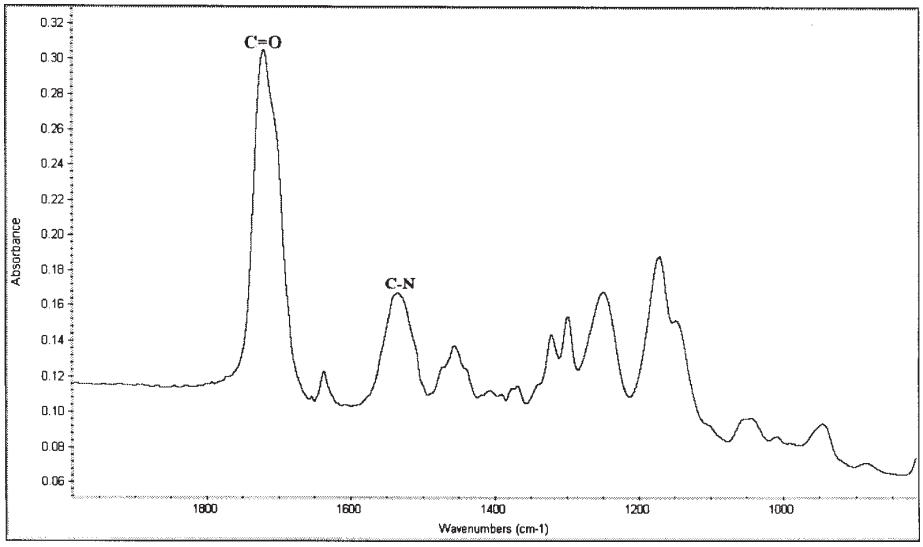


Fig. 2. FTIR spectrum of copolymer Standard 2

spectrometry. Thus, six standard solutions, based on different concentrations of BisGMA and UDMA in methanol were prepared to cover the whole range of concentrations (table 1).

A characteristic peak from UDMA monomer at 1532 cm^{-1}, corresponding to C-N bond, and the reference peak from 1720 cm^{-1}, assigned to C=O were chosen (fig. 2).

For each concentration, these two absorption bands were integrated (table 1) and from peak area the calibration curve A_{1532}/A_{1720} against UDMA concentration was plotted (fig. 3).

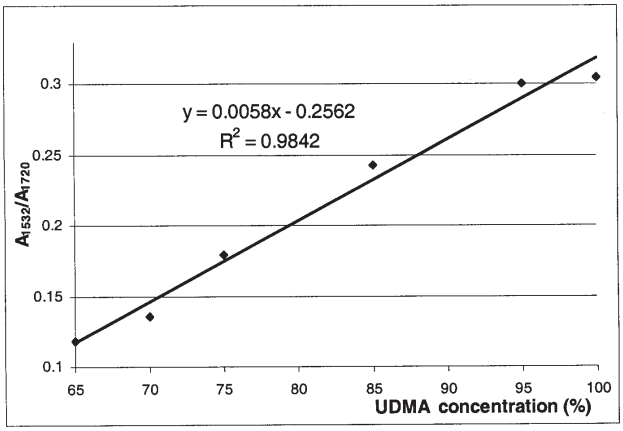


Fig. 3. The calibration curve A_{1532}/A_{1720} against UDMA concentration

Results and discussions

Using the calibration curve and the recorded FTIR spectra the concentrations of unreacted monomers were determined. The obtained concentrations help us to estimate, at certain times of reaction, the conversions for each of the two monomers in substrates S_1, S_2, S_3. (table 2, fig. 4 a), b), c)).

Using the obtained conversions the monomer reactivity ratios were calculated.

Copolymerization was assumed to obey a terminal model, meaning that only the monomer unit at the end of the propagating chain affected the kinetics. The reactivity ratios were estimated by using the copolymerization Mayo-Lewis equation [9]:

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1[M_1]^2 + [M_1][M_2]}{r_2[M_2]^2 + [M_1][M_2]} \quad (1)$$

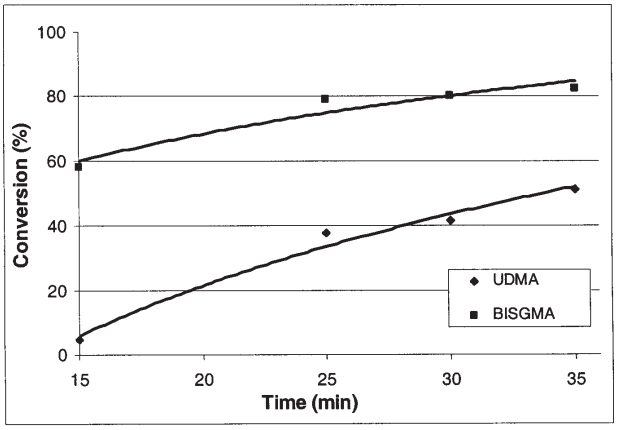
where:

Table 1
STANDARD SOLUTIONS PREPARED AND RATIO OF FT-IR ABSORPTIONS

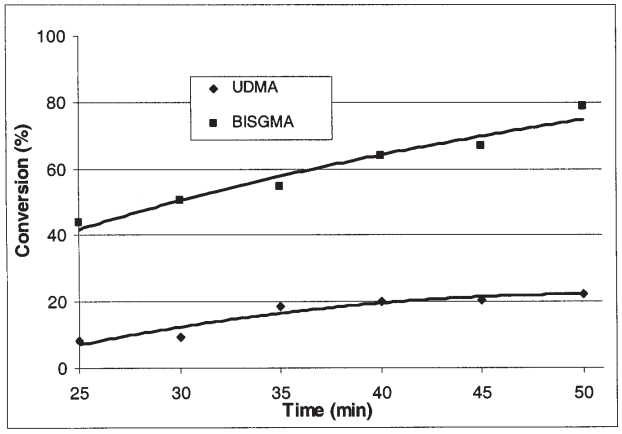
Standard No.	UDMA (%)	BisGMA (%)	A_{1532}/A_{1720}
1	100	-	0.305
2	95	5	0.3
3	85	15	0.243
4	75	25	0.179
5	70	30	0.136
6	65	35	0.118

Table 2
VALUES OF MONOMER CONVERSIONS

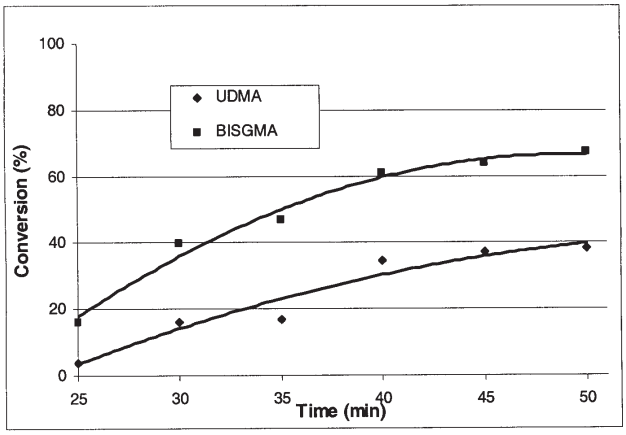
Conversion (%) / Time (min)	S_1		S_2		S_3	
	UDMA	BisGMA	UDMA	BisGMA	UDMA	BisGMA
15	4	58	-	-	-	-
25	38	79	8	44	4	16
30	42	80	9	50	16	40
35	51	83	19	55	17	47
40	-	-	20	64	35	61
45	-	-	21	67	37	64
50	-	-	23	79	38	67



a)



b)



c)

Fig. 4. Monomer conversions versus time for the system: a)S_1; b) S_2; c) S_3

where:

$$r_i = \frac{k_{ii}}{k_{ij}}; \quad (i = 1, 2; j = 2, 1); \tag{2}$$

$[M_1]$ and $[M_2]$ are the concentrations of the monomers at time t, $d[M_1]/d[M_2]$ is the ratio of the rates for monomer consuming during the process, r_1 and r_2 are the reactivity ratios for M_1 and M_2; k_{ii}, k_{ij} = constant rates.

In order to investigate and compare the experimental values r_1 and r_2, the dimethacrylates monomers reactivities were determined by using two conventional linearization methods. These two approaches were based on Fineman - Ross equation and copolymer composition equation respectively [9].

a)Fineman – Ross (FR) method

This method was first proposed as a graphic method by Fineman and Ross [9]. According to this method the differential form of Mayo-Lewis composition equation can be written as follows:

$$\frac{f}{F}(F - 1) = r_1 \frac{f^2}{F} - r_2 \tag{3}$$

$$\frac{F - 1}{f} = r_1 - r_2 \frac{F}{f^2} \tag{4}$$

where:

$$f = \frac{M_1}{M_2} \tag{5}$$

$$F = \frac{dM_1}{dM_2} \tag{6}$$

The graphic representation of f(F-1)/F as a function of (f^2/F), according to equation (3), gives a straight line with the slope equal to r_1 and intercept equal to - r_2 (fig. 5).

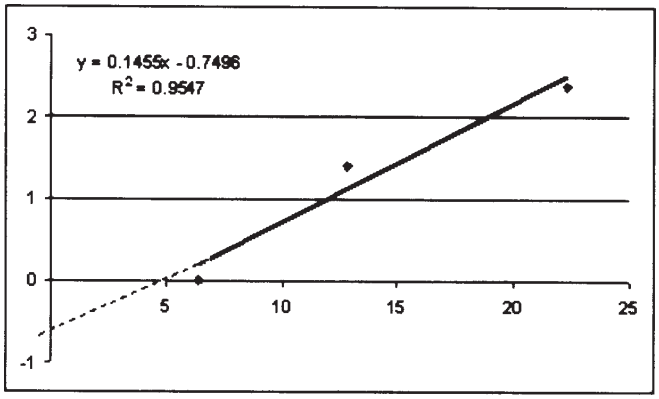


Fig. 5. The Fineman-Ross graphic representation

The equation composition (3) can be written as:

$$y = r_1 x + r_2 \tag{7}$$

where:

$$y = \frac{f}{F}(1 - F) \tag{8}$$

$$x = -\frac{f^2}{F} \tag{9}$$

The experimental values r_1 and r_2 obtained by FR method are:

r_1(UDMA) = 0.145
r_2(BisGMA) = 0.749

b) Copolymer composition equation

This second method uses the following equation [9]:

$$F = \frac{r_1 f^2 + f}{r_2 + f} \tag{10}$$

Table 3
REACTIVITY RATIOS OF (UDMA/BisGMA) SYSTEM

Linearization method based on	r_1(UDMA)	r_2(BisGMA)	$r_1 \times r_2$
Fineman Ross equation	0.145	0.749	0.108
copolymer composition equation	0.139	0.870	0.121
Average reactivity	**0.142**	**0.809**	**0.115**

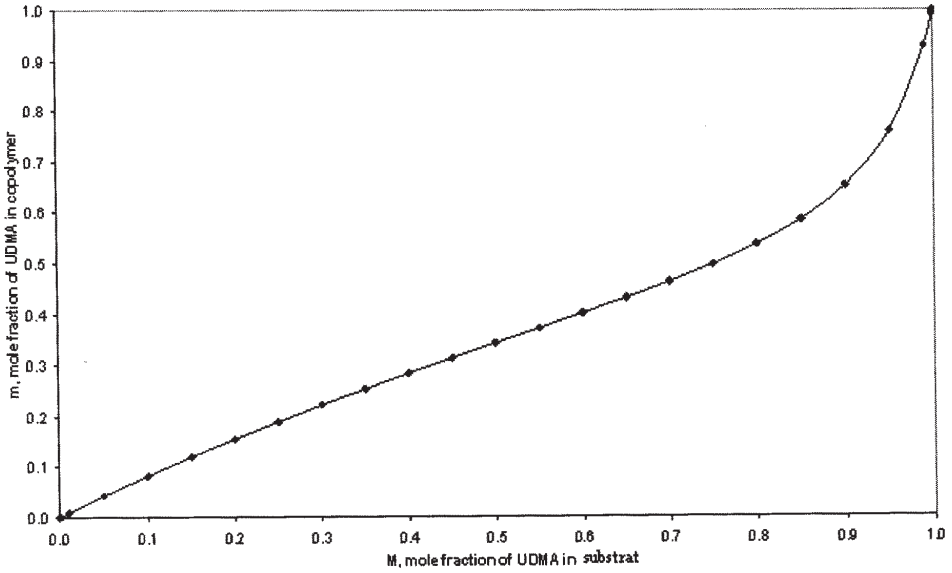


Fig. 6. The UDMA-BisGMA composition diagram

where:

$$f = \frac{M_1}{M_2} \quad (11)$$

$$F = \frac{dM_1}{dM_2} \quad (12)$$

In equation (10) r_1 and r_2 are unknowns, because, in a given experiment, f and F are determined from copolymer analysis. For an experiment i = 1, 2, 3 a.s.o., equation (10) takes the form:

$$r_1 \frac{f_i^2}{F_i} - r_2 + \frac{f_i}{F_i}(1 - F_i) = 0 \quad (13)$$

A system with two unknowns (r_1 and r_2) is thus obtained. The experimental values r_1 and r_2 obtained by copolymer composition method are:

r_1(UDMA) = 0.139
r_2(BisGMA) = 0.870

Table 3 lists the numerical values of r_1 and r_2 determined by the two methods and ($r_1 \times r_2$) which indicates the nature of the copolymer sequence.

It is well known that Fineman Ross equation is applied for conversions lower than 10%. Even if our data correspond to higher conversion, the r_1 and r_2 values obtained from Fineman Ross equation are comparable with those produced from the equation of copolymer composition. However for predicting reliable data we used the method described in [11] which is in fact a multifunctional application developed to solve the main problems related to the conversion effect against the reactivity ratios estimation methods.

Recently, these researchers have used the same ProCop computer program to analyze the experimental data from ten different copolymerization systems. They proved that the differences between the values of reactivity ratios initially published and the recalculated values can be discussed in terms of many factors such as experimental errors, analytical methods, conversion values and the solvent effect [12].

Considering that both methods used to calculate the reactivity ratios are linear, the obtained experimental data were introduced and reviewed in ProCop computer program. ProCop computes the reactivity ratios using non-linear Tidwell-Mortimer method, which involves all the experimental data including conversion values. Non-linear methods are the most reliable statistical analyses of copolymer composition data while linear methods only offer a qualitative estimate of precision [13, 14].

In the analysed substrates S_1, S_2, S_3 the values of reactivity ratios obtained by using ProCop computer program are:

r_1(UDMA) = 0.125
r_2(BisGMA) = 1.151

Computer program ProCop developed by C. Hagiopol was also used to predict copolymer compositions. The composition diagram showing the instantaneous copolymer composition (m_1) against the substrate composition (M_1) is shown in figure 6.

Regardless of the method by which the reactivity ratios were calculated, r_2 is greater than r_1, indicating that the BisGMA monomer preferentially entered the copolymer at early reaction stages.

Conclusions

The values of the reactivity ratios for the UDMA-BisGMA comonomers system were calculated starting from the FT-IR spectra.

Both Fineman Ross linearization method and copolymer composition equation were used to find the r_1 and r_2 values. The value of r_1 indicates that the UDMA monomer is more likely to give copolymerization with BisGMA than homopolymerization. However, the product of r_1 and r_2 is

less than 1, which clearly indicates that the system forms a statistic copolymer.

Tidwell-Mortimer is a non-linear least-squares method of estimating reactivity ratios and it best characterizes the system UDMA-bisGMA.

The reactivity ratios for UDMA-BisGMA system were also estimated from a model based on non-linear Tidwell-Mortimer method giving similar results but a higher value of r_2 than for linear methods.

Acknowledgement: Financial support from National University Research Council, PCE project, code 1718.

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Manuscript received: 12.11.2010