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Reactivity of a polymerizable amine activator in the free radical copolymerization with methyl methacrylate and surface properties of copolymers

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The relative reactivity of a polymerizable tertiary amine in free radical polymerization is analysed through the study of its copolymerization with methyl methacrylate initiated by benzoyl peroxide at low temperature. Copolymers of N,N-dimethylaminobenzyl methacrylate with methyl methacrylate were prepared in solution at low temperature (30 and 35°C) by using the polymerizable acrylic amine/BPO redox system as initiator. The reactivity ratios were calculated according to the general copolymerization equation from composition data of copolymer samples determined by ^{1}H n.m.r. spectroscopy, and by using both linearization methods and the non-linear least square analysis of Tidwell and Mortimer. The values obtained indicated that this system approaches to the ideal behaviour. Wetting experiments were carried out at room temperature in air to determine the surface energy of the copolymers. It was found that the surface energy increased with the content of N,N-dimethylaminobenzyl methacrylate in the copolymer, the copolymers becoming more hydrophobic as the fraction of this monomer increased in the copolymer. © 1997 Elsevier Science Ltd.

INTRODUCTION

Tertiary aromatic amines are the most commonly used activators of the benzoyl peroxide initiator for curing composite restorative resins and acrylic bone cements[1]. The most characteristic compound of this family, N,N-dimethyl-4-toluidine, DMT, is highly toxic, even by inhalation, and suspected carcinogen. Diffusion of the amine into the surrounding tissue is possible during the curing time of bone cements and dental composites which is between 2–10 min. Although less toxic amines have been recently studied for biomedical applications[2,3] some attempts have been made to develop new activators, which can be chemically incorporated into the polymerized materials, thus avoiding subsequent leaching[4-6]. The efficiency of the so-called 'polymerizable amines' in the redox system has been proved successfully. De Feng has found that this kind of system initiates the polymerization of methyl methacrylate and other vinyl monomers with a value of E_a close to that of BPO/DMT, i.e. $45 \pm 5\,\text{kJ}\,\text{mol}^{-1}$[7]. Recently, Si *et al.*[8] have investigated the use of a redox initiation system consisting of a polymerization amine and ammonium persulfate, for the aqueous polymerization of acrylamide, and they have found overall activation energies of the polymerization reaction in the same range (35–40 kJ mol^{-1}).

In previous papers we have demonstrated the efficiency of tertiary amines of reduced toxicity, N,N-dimethylaminobenzyl alcohol and N,N-dimethylaminobenzyl methacrylate, D, as activators in the redox initiation for the radical polymerization of methyl methacrylate, as well as their efficiency in the curing process of acrylic bone cements[9-11]. As is shown in *Scheme 1*, the molecular structure of the acrylic tertiary amine D contains the characteristic dimethylamino group linked to a 4-methylene aromatic ring, practically with the same electronic density and electronic cloud distribution than the traditional compound DMT, but in addition, a polymerizable methacrylic residue has been incorporated to the molecule in order to achieve a permanent covalent linkage between the amine and the polymeric backbone.

This paper deals with the study of the relative reactivity of N,N-dimethylaminobenzyl methacrylate by the analysis of the free radical copolymerization with methyl methacrylate in the range of temperature of practical interest (30–40°C). Also, wetting experiments were carried out in order to determine the surface energy of the copolymers.

EXPERIMENTAL

Materials

4-Dimethylaminobenzyl methacrylate, D, was synthesized[9,12] by the reaction of 4-dimethylaminobenzyl

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H_3C—N(H_3C)—⟨benzene⟩—CH_3

DMT

H_3C—N(H_3C)—⟨benzene⟩—CH_2—O—CO—C(CH_3)=CH_2

D
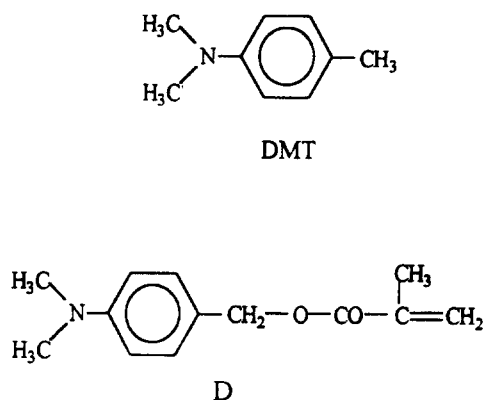
Scheme 1

alcohol with methacryloyl chloride (Fluka), at room temperature in the presence of triethylamine (Merck) as catalyst. 4-Dimethylaminobenzyl alcohol was previously synthesized[9,12] by selective reduction of 4-dimethylamino-benzaldehyde (Fluka) G with sodium borohydride (Merck) in alkaline medium. Methyl methacrylate, M (Merck), stabilized with 100 ppm of monomethylether of hydroquinone, was purified by distillation under nitrogen reduced pressure to remove the inhibitor.

Benzoyl peroxide, BPO (Merck), was purified by fractional recrystallization from ethanol, m.p. = 104°C. The solvents diethyl ether (Quimicen) S and N,N-dimethyl formamide (Scharlau) S and isopropanol (Normasol V) were used as received without further purification.

Methods

The copolymerization reaction was carried out in solution of N,N-dimethyl formamide $(1\,\mathrm{mol\,l^{-1}})$ at two different temperatures, 30 and 37°C, using the amine/BPO redox system as initiator. The BPO concentration was maintained constant in all the experiments (1.25% wt/wt with respect to monomer). The solutions of the monomers were degassed with oxygen-free nitrogen for 15 min. The ampoule was tightly closed and kept in a thermostat at a constant temperature the desired time to obtain copolymers at low conversion (<5%). The reaction medium was precipitated in isopropanol. The copolymer samples were isolated, washed with cool methanol and dried at low pressure until constant weight.

Characterization

N.m.r. spectra were recorded with a Varian XL300 Spectrometer at room temperature using deuterated chloroform (5% wt/v) as solvent.

Ar = ⟨benzene⟩—CH_2—O—CO—C(CH_3)=CH_2
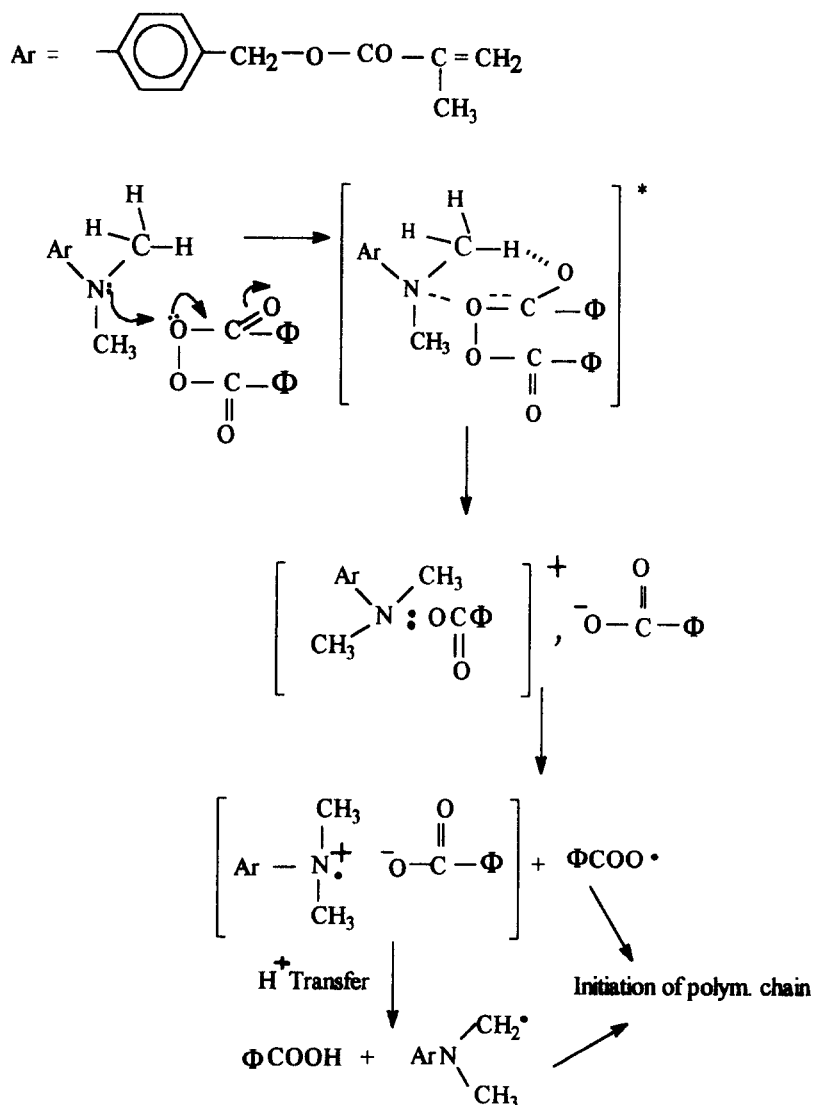
Scheme 2

The contact angle between liquid and solid surface was measured by means of a Contact Angle Measuring System G10 using the following procedure: a drop of a liquid was deposited on the surface to study. The liquids used for the experiments were distilled water and methylene iodide. The quantity of liquid was measured with a syringe monitored by a micrometric screw. The measurements were performed on films of copolymers at least ten times and the results were averaged.

RESULTS AND DISCUSSION

Copolymers of methyl methacrylate, M, with N,N-dimethylaminobenzyl methacrylate, D, were prepared by using a redox initiation system consisting of a polymerizable amine and benzoyl peroxide. The initiation mechanism of peroxy compounds and amine systems was studied by De Feng[7]. Results based on radical trapping and e.s.r. spectrum showed the formation of the N-methyl-4-toluidine methyl radical, and also the presence of the mentioned radical was detected by u.v. analysis of the polymer formed, indicating the efficiency of this radical in the initiation process. More recently, Si et al.[8] have studied the initiation mechanism of polymerizable redox systems based on ammonium persulfate by means of e.p.r., FTi.r., and u.v. spectroscopies. They proposed an initiation mechanism similar to that of the aliphatic tertiary amine/persulfate system, where both the alkylaminomethyl radical and the sulfate radical could initiate the free radical polymerization. Taking into consideration these suggestions, it could be considered that the D molecules participate actively in the free radical polymerization reaction, either in the initiation step through the radicals generated by hydrogen transfer from the N-methyl group and the benzoyl residue (*Scheme 2*) or as an acrylic polymerizable monomer through the addition of propagating free radicals to the acrylic double bond. If this mechanism is operative, the functionality of D molecules could be even higher than two, and those molecules participating in the initiation of an active polymer chain are able to participate also in the propagation step through the acrylic double bond. In this case, the process would give rise to the formation of branched polymeric and eventually crosslinked systems[4]. In fact, Hrabak et al. found that the copolymerization of 3- and 4-dimethylaminobenzyl methacrylates with styrene or methyl methacrylate using AIBN as initiator at 50°C, gave rise to crosslinked copolymers[12]. Likewise, we have observed the formation of insoluble polymers when D is polymerized in bulk even at room temperature. However, statistically the formation of primary N-methyl radicals is not favoured because of the relatively low concentration of benzoyl peroxide in the medium, particularly if the reaction is carried out in diluted solution. Therefore, in order to avoid gelation and crosslinking, the copolymerization reactions of this monomer with methyl methacrylate were performed in solution, at relatively low molar concentration of the monomers (1 mol l^{-1}) and, in addition, they were terminated at low conversions (<5%). A first series of copolymers was obtained at 30°C. A second set of copolymers was prepared at the temperature of the physiological medium (37°C), considering the potential use of this system in biomedical applications. Copolymer composition was calculated from the ^{1}H n.m.r. spectra of the copolymer
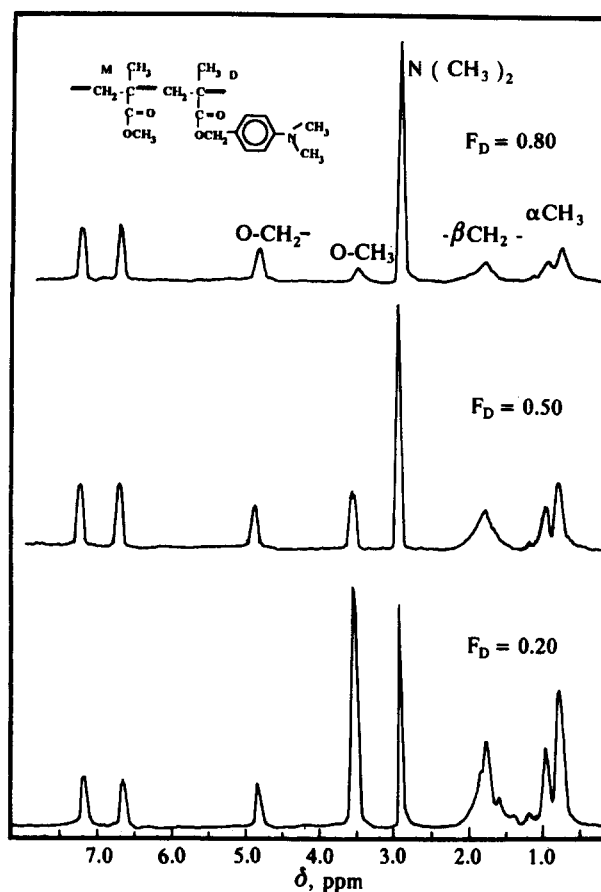

Figure 1 ^{1}H n.m.r. spectra of D/M copolymers of different composition in deuterated chloroform

Table 1 Average composition and conditional probabilities of D/M copolymers prepared in solution with the amine/BPO redox system as initiator at two different temperatures. [BPO] = 1.25 wt%

F_D (feed)	f_D (copol.) obtained at 30°C	f_D (copol.) obtained at 37°C	P_{DM}	P_{MD}
0.200	0.20$_7$	0.21$_2$	0.76	0.22
0.400	0.43$_4$	0.45$_8$	0.53	0.43
0.500	0.54$_9$	0.55$_4$	0.43	0.53
0.600	0.64$_3$	0.64$_5$	0.34	0.63
0.800	0.82$_8$	0.84$_2$	0.16	0.82

samples isolated at low conversion. *Figure 1* shows the spectra of three copolymer samples prepared with 20, 50 and 80 mol% of D in the feed. The integrated intensity of signals assigned to the N(CH$_3$)$_2$ (δ = 2.90), O–CH$_2$ (δ = 4.85) and aromatic protons (δ = 6.70 and 7.20 ppm) was compared with that of the OCH$_3$ (δ = 3.55) of M units incorporated to the macromolecular chains. The data were averaged and the results obtained at both polymerization temperatures are summarized in *Table 1*. Considering the limit of error in the estimation of data from ^{1}H n.m.r. spectroscopy, it can be considered that the average composition of copolymer chains does not change with the temperature in this interval. Therefore, it is clear that there is not any noticeable effect of the thermal initiation in the polymerization process. On the other hand, it is clear that the average composition of copolymer chains is very similar to that of the initial monomer feed. The conditional probabilities P_{ij} (i, j = D, M) defined[13] as the probability for the addition
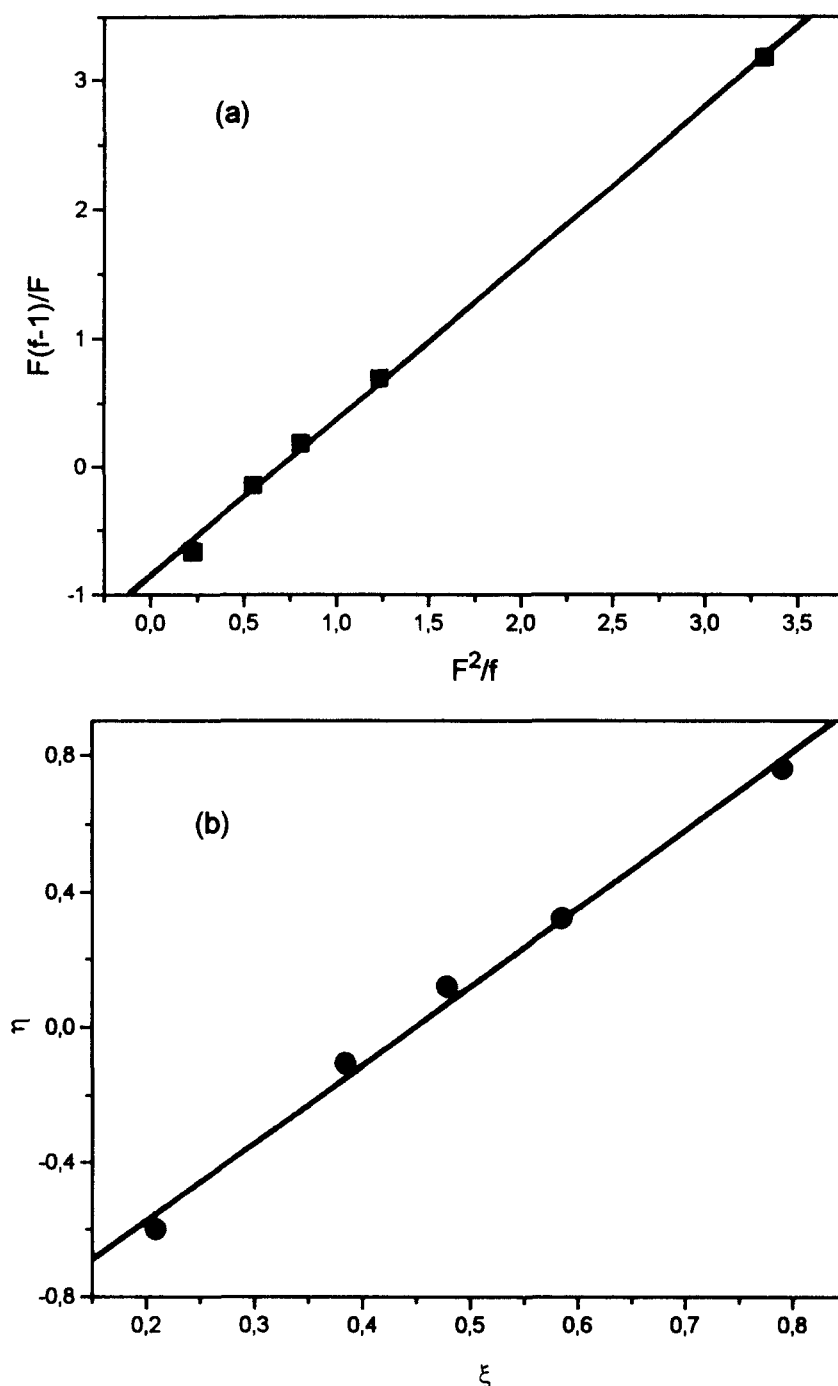
Figure 2 Diagrams of Fineman–Ross (a) and Kelen–Tudos (b) for the radical copolymerization of D with M, in solution at 30°C initiated by the amine/BPO redox system

of monomer units j to free radical i ends, were calculated statistically from the best values of the corresponding reactivity ratios.

The values of the reactivity ratios were determined by using the Fineman–Ross[14] (*Figure 2a*) and Kelen–Tudos[15] (*Figure 2b*) linearization methods, as well as by the application of non-linear least square analysis suggested by Tidwell and Mortimer[16]. Also, the application of the mathematical treatment suggested by Behnken[17] and Tidwell and Mortimer[16] provided the elliptical diagram drawn in *Figure 3* which shows the so-called 95% confidence limit, indicating that the values of reactivity ratios obtained by the non-linear least square analysis are the most appropriate values to be used. The values of r_D and r_M determined by the three methods are quoted in *Table 2*. Hrabák *et al.*[12]

Table 2 Reactivity ratios of the free radical copolymerization of D/M pair in N,N-dimethylformamide at 30°C initiated by the amine/BPO redox system. [BPO] = 1.25 wt%

Method	r_D	r_M	$1/r_D$	$1/r_M$	$r_D \times r_M$
F–R	1.22 ± 0.03	0.85 ± 0.05	0.82	1.18	0.96
K–T	1.27 ± 0.19	0.91 ± 0.06	0.79	1.10	1.15
T–M	1.30	0.88	0.77	1.13	1.14

reported Q and e values for the 4-dimethylaminobenzyl methacrylate of $Q = 0.70$ and $e = 0.40$. According to the classical relationship of these parameters with the reactivity ratios[18] and taking into consideration the Q and e values of methyl methacrylate ($Q = 0.74$ and $e = 0.40$) reactivity ratios of $r_D = 0.94$ and $r_M = 1.06$ are
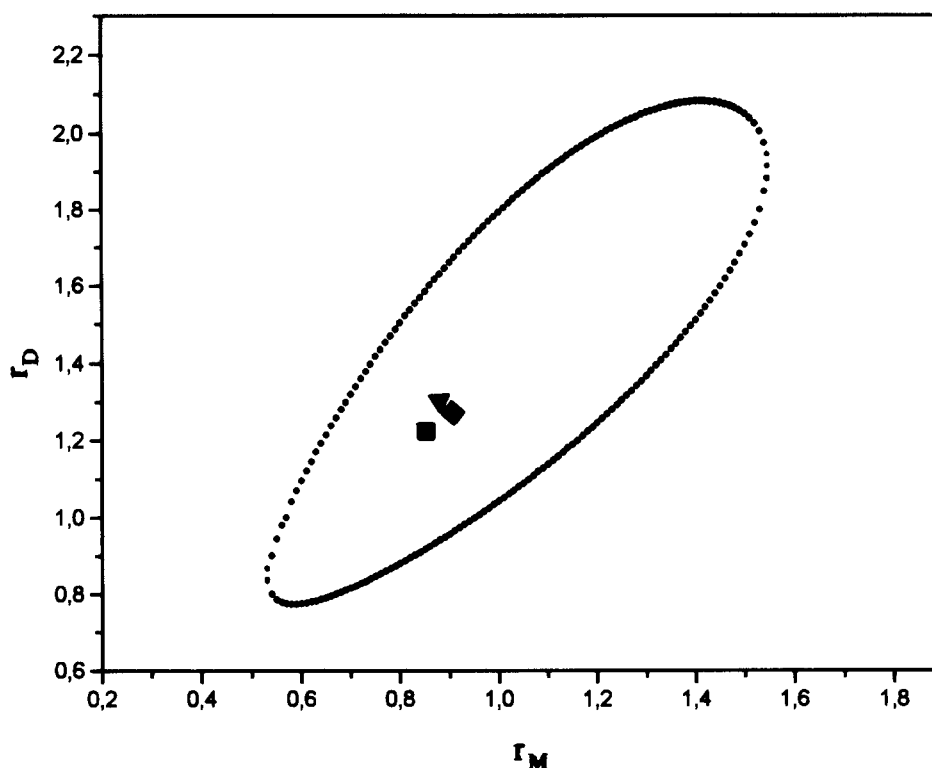
Figure 3 95% Confidence diagram for the reactivity ratios of D and M, determined by the non-linear least-squares method suggested by Tidwell and Mortimer. Values of reactivity ratios: (▼) Tidwell-Mortimer; (◆) Kelen–Tudos; (■) Fineman–Ross
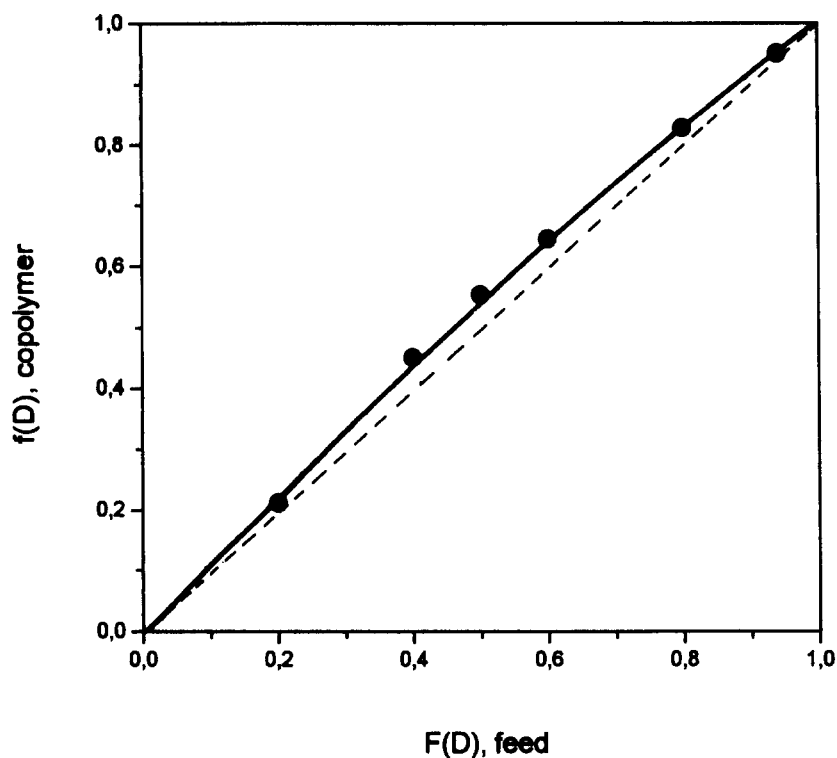

Figure 4 Composition diagram for D/M copolymerization system

obtained. These values are very close to those obtained from the experimental compositions analysed in this work. The application of these results to the Mayo–Lewis[19] equation gives the copolymer composition diagram shown in *Figure 4*, where the experimental points fit the corresponding composition diagram calculated from the reactivity ratios determined by the Tidwell–Mortimer method. According to these results,

as can be observed in *Table 2*, the product r_D by r_M is very close to the unity, indicating that the copolymerization approaches to the ideal behaviour with a random distribution of monomeric units along the copolymer chains. It can be observed that the growing chains ending in D radicals present slightly higher reactivity towards M monomer molecules than towards its own monomer, D. These results demonstrate the ability of D monomer to
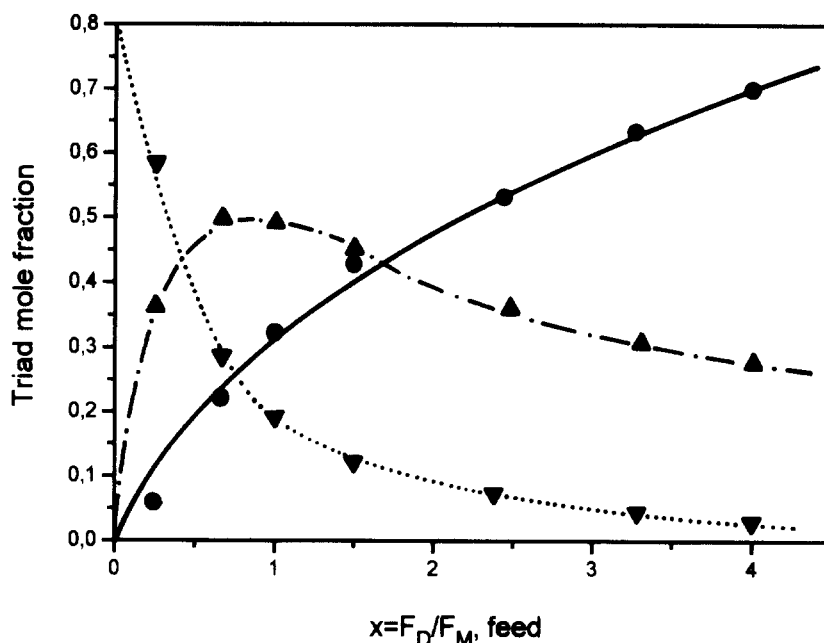
Figure 5 Content of D centred triads as a function of the N,N-dimethylaminobenzyl methacrylate mole fraction in the copolymer for the copolymerization of this monomer with methyl methacrylate. (●) DDD triads; (▲) DDM + MDD; (▼) MDM triads

copolymerize with methyl methacrylate, and therefore, the incorporation of D molecules into the macro-molecular chains when low quantities of this monomer are present in the polymerization reaction of methyl methacrylate, i.e., acrylic bone cements formulations.

Figure 5 shows the statistical diagrams of D centred sequences in terms of triads determined from the reactivity ratios by the Tidwell and Mortimer method according to the classical Mayo–Lewis model. The distribution of D centred sequences depends on the average composition of copolymer chains. The mole fraction of alternating MDM triads decreased drastically with D mole fraction in the copolymer, whereas the mole fraction of homotriads DDD increased smoothly. However, the mole fraction of heterotriads having two D units reaches a wide maximum at about $f(D) = 0.5$.

On the other hand, the interfacial characteristics of polymeric systems in contact with hydrated media are important to predict the interactions of this kind of material with the surrounding tissues when they are applied in the human body. These parameters in general are determined by means of wetting experiments being the sessile drop technique one of the most usual. In this work we applied the sessile drop technique at room temperature in air to determine the surface energy of the copolymers. The contribution of the dispersion and polar interactions to the surface energy was determined considering that the intermolecular attraction which causes surface energy γ, results from a variety of intermolecular forces according to an additive rule. Most of these forces are functions of the specific chemical nature of a particular material, and the surface energy can be compiled as γ^p (polar interactions). On the other hand, dispersion forces (γ^d) are always present in all systems independently of their chemical nature. Thus, the surface energy of every system, solid or liquid, may be described by

$$\gamma = \gamma^d + \gamma^p \qquad (1)$$

Fowkes[20] has derived from the Young equation an expression for the contact angle of a liquid on a solid in terms of the dispersion force contributions of each

$$1 + \cos\theta = 2[(\gamma_s^d)^{1/2}(\gamma_l^d)^{1/2}]/\gamma_l \qquad (2)$$

where γ_s^d is the dispersive energy of the solid, γ_l^d is the dispersive energy of the liquid, γ_l is the free interfacial energy of the liquid and θ is the contact angle. In cases where only dispersion forces operate, i.e. the liquid or solid is non polar, it is possible to approximate γ_s^d from a single measurement of the contact angle by the use of equation (2). For cases where both forces operate Owens[21] suggested a more general form of this equation which can be written as

$$1 + \cos\theta = 2[(\gamma_s^d)^{1/2}(\gamma_l^d)^{1/2}]/\gamma_l + 2[(\gamma_s^p)^{1/2}(\gamma_l^p)^{1/2}]/\gamma_l \qquad (3)$$

Thus, it is possible to determine the free energy surface of a solid and its dispersive and polar components by using two liquids of very different properties. Owens *et al.* considered this method especially applicable to the surface characterization of polymers, and they reported the free energy values for some polymers[21]. More recently, Nakamae *et al.* have applied this method to determine the surface characteristics of copolymers based on methyl methacrylate and a monomer bearing a pendant glucose unit, and copolymers of methyl methacrylate and 2-hydroxyethyl methacrylate[23]. In this study the dispersive γ_s^d components of the copolymers were determined by measuring the contact angle of methylene iodine, which has a surface free energy of $51.0 \, \text{mN m}^{-1}$ only due to dispersive forces. The polar γ_s^p components of the copolymers were determined using water as solvent which has a dispersive component of 21.8 and a polar component of $51.0 \, \text{mN m}^{-1}$. There was observed a decrease in the contact angle of methylene iodine with increasing the content of D in the copolymer (*Table 3*) which indicates that the surface of the copolymer films becomes hydrophobic. *Table 3* also shows the values of surface energy obtained for copolymer samples of different composition together

Table 3 Mean values of contact angles, θ, at room temperature in air and values of surface energy, γ_s, with its dispersive, γ_s^d, and polar, γ_s^p, contributions, and of critical surface tension γ_c, for D/M copolymers with different composition, for poly(N,N-dimethylaminobenzyl methacrylate), PD, and for poly(methyl methacrylate), PM

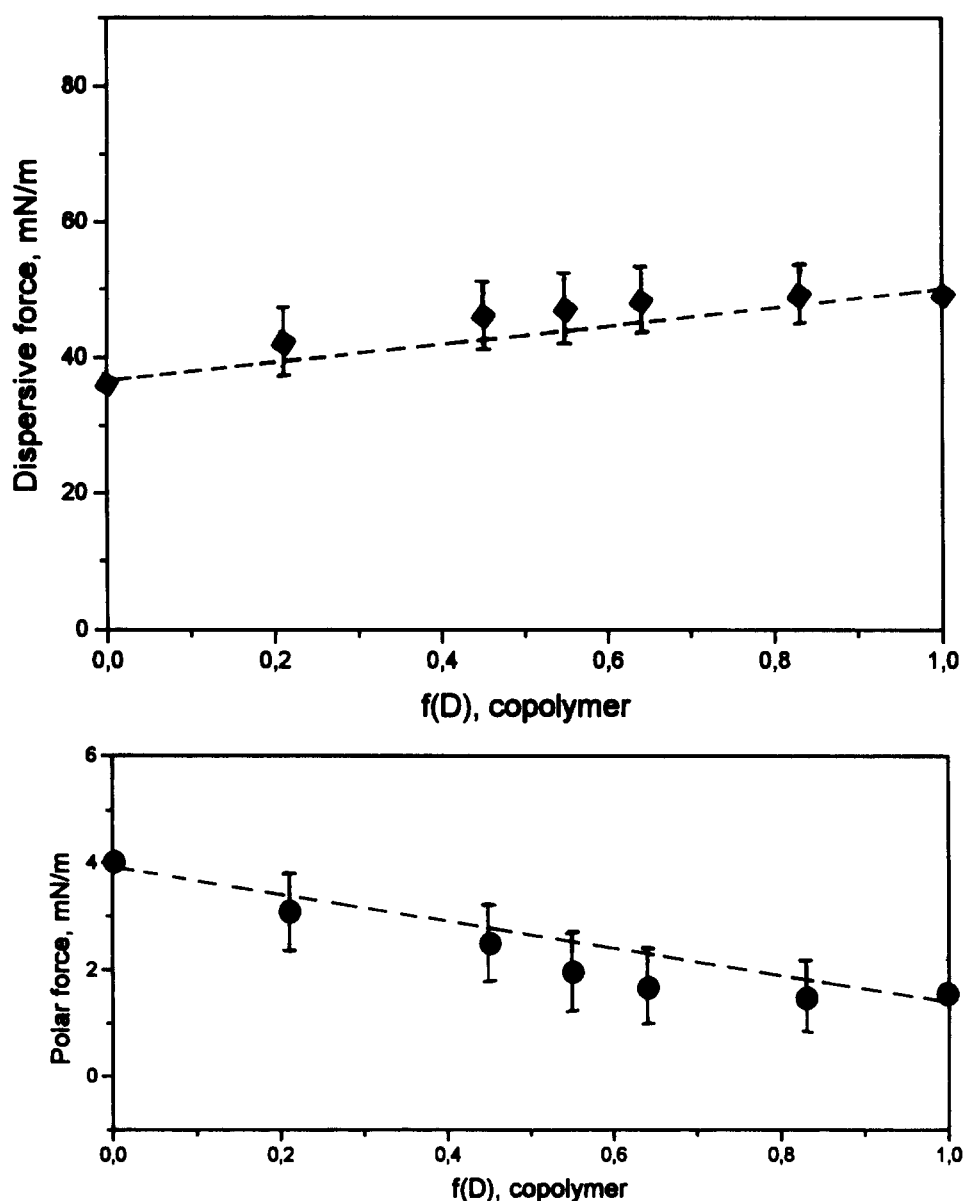| f (D) copolymer	Contact angle, $\theta°$ water	Contact angle, $\theta°$ methylene iodide	γ_s (mN m^{-1})	γ_s^d (mN m^{-1})	γ_s^p (mN m^{-1})	γ_c (mN m^{-1})
PM*	80	40	40	36	4	39
0.21	80	35	45	42	3.0	43
0.45	81	26	48	46	2.4	48
0.55	82	22	49	47	1.9	49
0.64	82	19	50	48	1.6	49
0.83	82	17	50	49	1.4	50
PD	82	16	51	49	1.5	50

Figure 6 Variation of the dispersive γ_s^d and polar γ_s^p components of the surface energy with the content of D for D/M copolymers of different composition

with those obtained for poly(dimethylaminobenzyl methacrylate) (PD) prepared in the same experimental conditions. The values reported in the literature for poly(methyl methacrylate)[21] are also included. It was found that the surface energy of copolymers increased

with the content of D in the copolymer composition. This increase was due to a rise of dispersive contributions as the content of D monomer was higher since the polar forces decreased slightly. The contribution of the aromatic amine group to the overall increase of surface energy

respect to that of the pure poly(methyl methacrylate) chains seems to be additive, considering the average composition of the copolymer system and the fractional contribution of each component. As it is observed with other physical and physicochemical properties of polymer chains and copolymeric systems, it is rather frequent to find a simple additive contribution of groups or specific functions to one characteristic property[23]. Accordingly, we could consider that the dispersive or the polar components of the surface energy are the fractional contribution of the parameters of the corresponding homopolymers which can be determined by the equations:

$$\gamma_s^d = \gamma_D^d f(D) + \gamma_M^d f(M) \tag{4}$$

$$\gamma_s^p = \gamma_D^p f(D) + \gamma_M^p f(M) \tag{5}$$

where γ_D^d and γ_D^p are the surface energy components of poly(N,N-dimethylaminobenzyl methacrylate), PD; γ_M^d and γ_M^p those of the poly(methyl methacrylate) and $f(D)$, $f(M) = 1 - f(D)$ the molar fraction of each kind of monomeric units in the copolymer chains. *Figure 6* shows the diagrams obtained with this approximation; the lines correspond to the variation of γ_s^d and γ_s^p according to the equations (4) and (5) with a good fitting of the experimental data, which supports the validity of the treatment.

Zisman and coworkers[24] found that a plot of $\cos\theta$ vs γ_l for homologous series of liquids on a given solid is a straight line generally, and have introduced the concept of critical surface tension of wetting (γ_c). This empirical quantity is defined as the value of γ_l at the intercept of the plot of $\cos\theta$ vs γ_l with the horizontal line, $\cos\theta = 1$. Liquids of γ_l less than γ_c would be expected to spread on the solid surface. This treatment was applied for the D/M copolymers and the results are collected in the seventh column of *Table 3*.

CONCLUSIONS

The reactivity of the polymerizable tertiary amine, D, in the free radical polymerization initiated by benzoyl peroxide at low temperature has been demonstrated by the copolymerization of D with methyl methacrylate.

Pure random copolymers in the experimental conditions of this work are obtained with reactivity ratios $r_D = 1.30$ and $r_M = 0.88$.

The adhesion properties of the copolymer system in a wide composition interval were analysed by the measure of contact angle with liquids of different polarity, i.e. water and methylene iodide, indicating a relative increase of the hydrophobic character of the system with the content of D. In addition, the results obtained show that the dispersive and the polar components of the surface energy are additive fractional contribution of the parameters for the corresponding homopolymers.

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