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Reactivity of Radicals Derived from Dimethylanilines in Acrylic Photopolymerization

J. L. Mateo,* P. Bosch, and A. E. Lozano

Instituto de Polímeros, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain

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ABSTRACT: Relative reactivities of radicals derived from several *p*-dimethylanilines toward the polymerization of butyl acrylate have been calculated. It was observed that the reactivity of the radicals increases as the electron-withdrawing character of the groups attached in the para position increases. The experimental efficiency factor (*f*) has been found to be proportional to the σ_p value defined in the Hammett equation. The dependence of the reactivities on the nature of the radicals has also been explained through their frontier orbital characteristics. The high similarity of the behavior of *f* versus σ_p and *f* versus E_{SOMO} led us to conclude that the simple perturbative molecular orbital calculations can be used to predict the relative reactivity of initiating radicals with similar structure toward the polymerization of acrylic monomers.

Introduction

Tertiary amines are the most widely used coinitiators for photoinitiated radical polymerization, being the source of the radicals which actually start the growth of the polymer chain. Even so, little has been done to study the relationship between the reactivities and the chemical structures of these radicals toward acrylic monomers. Given that amines take part in the reaction through reduction of the excited state of an aryl ketone photoinitiator¹ (electron transfer followed by a proton transfer), some authors have correlated the experimental order of reactivity with their reduction kinetic constant² or the experimental quantum yield of photoreduction with the ionization potential of the amines.³ Other unexplained acceleration or retardation effects in rates of polymerization were described as "synergistic" and "antagonistic".

In previous studies of the polymerization of acrylic monomers using conjugated and nonconjugated aminobenzophenones as photoinitiators,⁴ we have determined the nature and the efficiency of the generated radicals. It was concluded that the overall rate of polymerization was a function of the product ($\Phi_{\text{ex}}f$), where Φ_{ex} is the experimental quantum yield of photoinitiator photoreduction and *f* is the efficiency of the initiating radicals. The radical efficiency value of the conjugated aminobenzophenone molecule studied (4-isopropyl-4'-(dimethylamino)benzophenone) toward acrylic monomers was about 80 times higher than the value for a nonconjugated aminobenzophenone (4-[2'-(diethylamino)ethoxy]benzophenone). Then, the similar rates of polymerization obtained for MMA polymerization using these two photoinitiators under identical irradiation absorption intensities was explained by the fact that the much higher rate of radical production of the unconjugated aminobenzophenone was compensated by the much higher reactivity of the radical derived from the conjugated aminobenzophenone.

In Table 1 are given the absolute efficiencies of different radicals obtained from the above studies. Relative efficiencies for other related radicals obtained from data in the literature⁵ are also included.

The aim of the present article is to compare the

Table 1. Efficiencies of Initiating Radicals in Solution Polymerization of MMA

radical	rel eff	radical	abs eff
PhCO [•]	1.0	cyclohexyl [•]	0.030
THF [•]	4.6	THF [•]	0.160
Et ₂ NCH [•] CH ₃	0.2	¹ PrC ₆ H ₄ COC ₆ H ₄ N(CH ₃)CH ₂ [•]	0.650
		PhCOC ₆ H ₄ O(CH ₂) ₂ N(Et)CH [•] CH ₃	0.008

efficiencies of radicals arising from some para-substituted dimethylanilines (Figure 1) and attempt to explain the dependence between the structure of the radicals (nature of the R substituent) and the radical reactivity.

Experimental Section

Materials. Benzene (spectroscopic grade from Merck) was used as received. Butyl acrylate (BA) from Fluka AG was purified by washing with diluted sodium carbonate solution followed by distilled water, then dried over magnesium sulfate, and finally distilled under reduced pressure. The purified monomer was stored in the dark at low temperature and redistilled before use.

Triethylamine (TEA) from Merck, *N,N*-dimethylaniline (DMA), and *N,N*-dimethyltoluidine (DMT) from Fluka AG were purified by distillation under reduced pressure and stored in the dark under nitrogen. 4-(dimethylamino)-4'-isopropylbenzophenone (DMAIB) was prepared according to the method previously described.⁶ Methyl 4-(dimethylamino)benzoate (DMAMB), 4-(dimethylamino)benzophenone (DMAB), and 4-(dimethylamino)benzonitrile (DMABN) were obtained from commercial suppliers (Fluka AG and Aldrich Chemical Co.) and recrystallized from ethanol-water mixtures.

Camphorquinone (Aldrich Chemical Co.) was used without further purification.

Irradiations. Photoreduction quantum yields of camphorquinone were measured under irradiation at $\lambda = 436$ nm in benzene and benzene-monomer solutions in the presence of equimolecular quantities of the amines mentioned above. The decrease in the camphorquinone absorption band was followed by a Shimadzu UV-265 FS spectrophotometer by taking readings of its maximum at $\lambda = 471$ nm at different times of irradiation. Solutions were previously deoxygenated by purging with nitrogen. Aberchrome 540 (Edward Davids Chemical Laboratories) was used as an actinometer to measure the absolute value of the light intensity for the incident monochromatic light.⁷

The polymerization study by differential scanning calorimetry (photo-DSC) was performed as described previously.⁸ All the irradiations were done at 40 °C in BA in bulk and under a nitrogen atmosphere. Sample quantities of 20 μ L were accurately measured using a Hamilton 25 μ L syringe. The samples were irradiated using visible cold light from a

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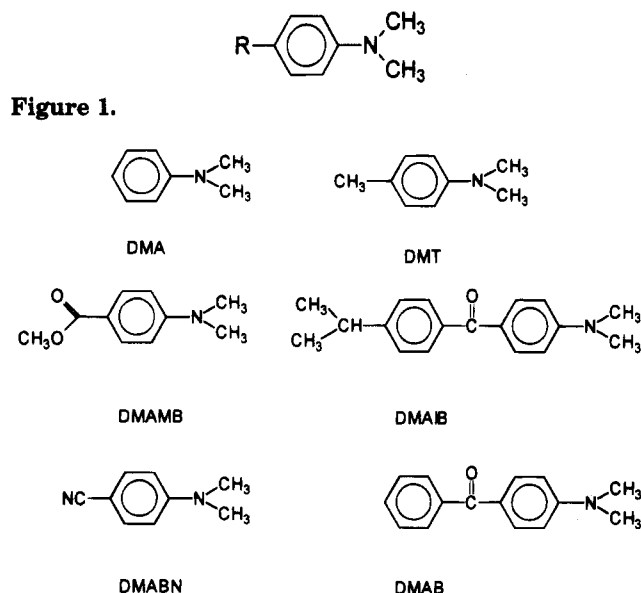


Figure 2. Structures of the dimethylanilines used as coinitiators.

Schott KL-1500 source filtered by a Schott DAL-434 filter (maximum transmission at 430 nm and half-band-pass of 18 nm).

Theoretical Calculations of Frontier Orbital Characteristics. Semiempirical calculations were performed using the original parameters of the program PM3,⁹ based on the unrestricted Hartree-Fock (UHF) method, included in MOPAC version 6.0.¹⁰ This semiempirical method is commonly accepted to allow a better description of the lone-pair/lone-pair repulsion in several compounds.¹¹ Thus, the calculation of hypervalent molecules and heterocyclic compounds has been improved with respect to other semiempirical calculations.¹² Furthermore, the results of PM3 on some selected molecules were checked with the program AM1, another semiempirical SCF-MO commonly used in theoretical studies of organic molecules.¹³ The results were always found to be comparable, giving the same differential reactivity. The program ran on a VAX 9210 computer at the Computer Center of CSIC (Consejo Superior de Investigaciones Científicas, Madrid, Spain).

Initial geometries were obtained by molecular mechanics (MM+) by means of the program Hyperchem version 3.¹⁴ The results of this optimization were employed as input data for the semiempirical calculations. The same program was used to visualize the structures obtained after MOPAC minimization.

Geometries were optimized in internal coordinates. The optimization was stopped when Herbert or Peter tests were satisfied by the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method. The PRECISE option was applied at the end of the optimization process.

Results and Discussion

The structures of the substituted *N,N*-dimethylanilines used in this work are shown in Figure 2. These tertiary amines were used together with camphorquinone as the photoinitiator system for the polymerization of butyl acrylate. According to the behavior under irradiation of the camphorquinone in the presence of amines,¹⁵ substituted dimethylamino radicals must be produced (exciplex formation by electron transfer followed by proton transfer) when these systems are irradiated at a wavelength where only the camphorquinone absorbs ($\lambda > 400$ nm). These radicals are responsible for the polymerization of the acrylic monomers as shown in Scheme 1.

According to the general equation for radical photo

Scheme 1. Photoreduction of Camphorquinone in the Presence of Amines

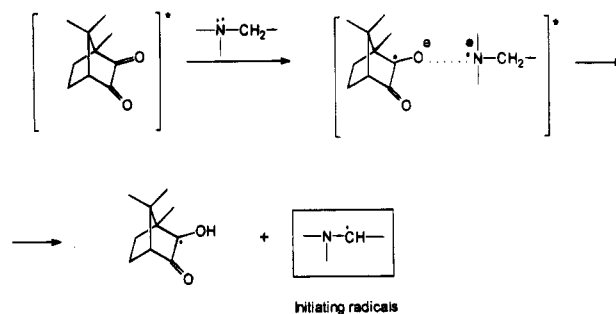


Table 2. Quantum Yields of Camphorquinone Disappearance Using Dimethylaniline Derivatives as Coinitiators in Benzene and Benzene-Monomer Solutions^a

DMA deriv	Φ_H in benzene	Φ_H in benzene-BA (1:1)
DMT	0.18	0.19
DMA	0.19	
DMAMB	0.18	0.17
DMAIB	0.17	
DMAB	0.16	
DMABN	0.17	0.16
triethylamine	0.42	

^a Molar ratio CQ/xDMA = 1; $I_0 = (0.8-0.9) \times 10^{-8}$ einstein s⁻¹; absorbance at 436 nm = 0.2-0.3; irradiation wavelength $\lambda = 436$ nm.

initiated polymerization

$$R_p = k_p/k_t^{1/2}[M]_a^{1/2}\phi_i^{1/2} \quad (1)$$

and considering that

$$\phi_i = \Phi_H f \quad (2)$$

where ϕ_i is the quantum yield for the initiation process, Φ_H is the disappearance quantum yield (photoreduction quantum yield), and f is the efficiency factor (fraction of active radicals that initiate polymerization), the R_p^2/Φ_H ratio value, when identical irradiation absorption intensities are used, will measure the efficiency factor of the corresponding radical [$f = R_p^2/\Phi_H$]. So, measuring these parameters, R_p and Φ_H , it will be possible to compare the efficiencies of the above radicals of the *N,N*-dimethylaniline derivatives.

Photoreduction Behavior and Rates of Polymerization. The photoreduction behavior of camphorquinone under irradiation at 436 nm by the dimethylaniline derivatives mentioned above in benzene and benzene-monomer solution was followed by the decrease in the camphorquinone band at its maximum of 471 nm. The results obtained are shown in Table 2 and indicate that the presence of the monomer used does not have an appreciable effect on the photoreduction quantum yield, and therefore no electronic charge transfer occurs from the camphorquinone triplet to the monomer ground state.

The kinetics of polymerization were monitored by DSC. Exotherm rates as a function of time were obtained under isothermal conditions (40 °C) for continuous illumination reactions. The polymerization started with neither inhibition nor retardation periods, and the polymerization rate values given in Table 3 correspond to the maximum values which were reached soon after the light was turned on (within about 15 s after opening the shutter), i.e., when the concentration of free radicals has reached the steady-state value and

Table 3. Rates of BA Polymerization Using Camphorquinone-xDMA as Photoinitiator System^a

DMA deriv	R_p (mcal/s)	R_p^2/Φ_H
DMT	0.9	4.5
DMA	1.2	7.6
DMAMB	2.3	27.4
DMAIB	2.8	46.1
DMAB	2.9	50.7
DMABN	3.2	60.2
triethylamine	1.0	2.3

^a Irradiation wavelength = 436 nm; molar ratio CQ/xDMA = 1; I_0 = 0.26 mcal/s; light absorbance at 436 nm = 0.2.

the concentration of residual monomer is the greatest. Rates of polymerization and experimental efficiencies are given in Table 3.

Here, important differences can be appreciated in the radical efficiencies of the dimethylaniline derivatives studied which only can be attributed to the nature of the parasubstituent of the aromatic ring. The radical reactivity seems to be a function of the electron-withdrawing character of the group attached in the para position with respect to the N atom. Also, all of the values are appreciably higher than the radical efficiency calculated for an aliphatic amine (triethylamine), which is in agreement with the results observed for polymerization in solution.⁴

Theoretical Study of the Differential Reactivities. The results obtained seem to indicate the existence of a relationship between the efficiency of the radicals and the nature of the dimethylaniline derivatives studied. Two types of correlation have been assessed:

(i) *Efficiency- σ_p values of the substituent*, as expressed by the Hammett equation:

$$\log(f/f_0) = \rho\sigma_p \quad (3)$$

(ii) *Efficiency-frontier orbital nature of the radicals*, as expressed by an expression similar to the Hammett equation.

(a) Radical Efficiency-Hammett parameter¹⁶ Correlation. It is known that the substituent effect on the rate of reaction is a composite function of polar ($\rho\sigma$), resonance (R), and steric (E_s) effects:

$$\log(f_x/f_0) = \rho\sigma_p + R + E_s \quad (4)$$

The steric effect, E_s , can be neglected in the present reaction. As an approximation, it can be assumed that the last equation can be transformed as follows:

$$\log f_x = \rho'\sigma_x + R_x \quad (5)$$

$$\log f_0 = \rho'\sigma_0 + R_0 \quad (6)$$

Accordingly, and given that $\sigma_0 = 0$, $\log(f_x/f_0)$ can be expressed by the equation

$$\log(f_x/f_0) = \rho'\sigma_x + (R_x - R_0) \quad (7)$$

If the difference in the resonance interaction between the two reactions is negligible [$(R_x - R_0) \rightarrow 0$], the linear relationship which is expected between $\log(f_x/f_0)$ and the σ_p values should pass through (0,0). This is found with the experimental values as shown in Figure 3, and the line of best fit passes through the origin, which confirms the absence of differential resonance effects. The σ_p values for all the derivatives have been taken

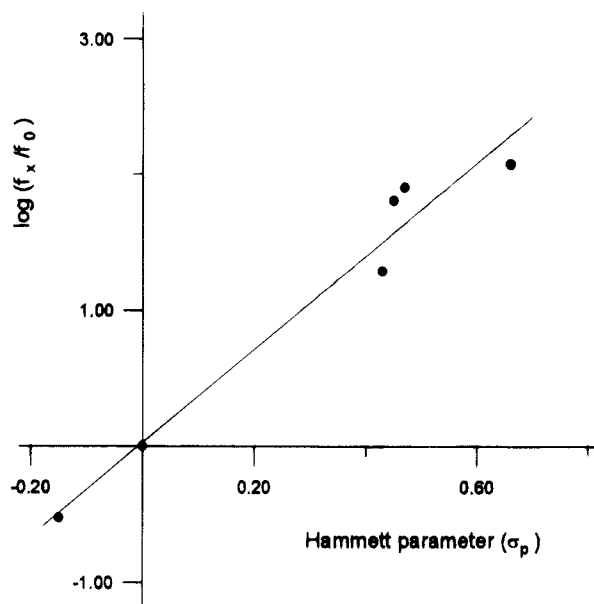


Figure 3. Plot of relative reactivity [$\log(f_x/f_0)$] vs Hammett parameter.

from ref 16, except that for DMAIB, which has been estimated.

(b) Dependence of Reactivity on the Frontier Orbital Characteristics. The quantum chemical calculation of the addition of free radicals to multiple bonds has received much attention in recent years.¹⁷ These reactions take place rapidly, having rate constants of the order 10^{-3} – 10^{-4} L mol⁻¹ s⁻¹ at ambient temperature and activation energies in the range 6 ± 2 kcal/mol.^{18,19} It has been determined experimentally that the addition of a radical to a double bond is controlled by thermodynamic factors, the exothermicity of the reaction being the determining factor in controlling the rate and the direction of addition. Dewar et al. studied, theoretically, the reactivity of a simple radical (CH_3^\bullet)²⁰ with several double bonds and stated that the steric effects are fundamental in determining the course that the radical reactions take. Thus, the radical attack takes place on the less hindered carbon of a double bond irrespective of the electronic characteristics of this double bond. Dewar also stated that the semiempirical quantum chemical methods could be useful in determining both the reactivity of radicals and the differential reactivity of distinct unsaturated molecules.

In a chemical reaction, the incipient interaction between two reactants starts initially with a small perturbation. Such small perturbation should correspond to small energy changes, which can be evaluated by perturbation expansion of the energy. This perturbation energy is expected to give a reliable indication of the energy in the initial stages of the reaction.²¹

Using quantum mechanical theory, an expression can be derived for the perturbation energy (ΔE) gained or lost when the orbitals of one reactant overlap with those of another.²² This equation, known as the Fukui-Klopman-Salem equation, has the following form:

$$\Delta E = -\sum_{ab} (q_a + q_b) \beta_{ab} S_{ab} + \sum_{k < l} \frac{Q_k Q_l}{\epsilon R_{kl}} + \sum_r \sum_s^{\text{occ unocc}} - \frac{2(\sum_{ab} c_{ra} c_{sb} \beta_{ab})^2}{E_r - E_s} \quad (8)$$

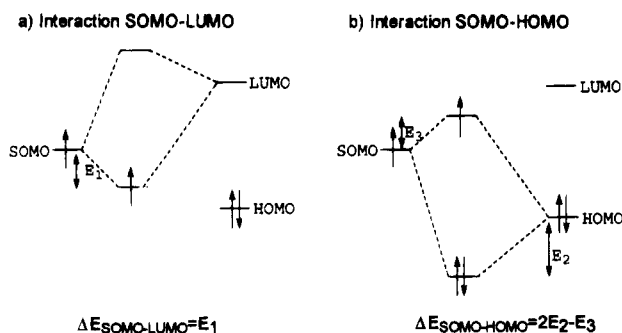


Figure 4. Scheme of the possible electronic interactions between the frontier orbitals of a radical and a molecule.

where q_a and q_b are the electron populations in atomic orbitals a and b , β and S are the resonance and overlap integrals, Q_k and Q_l are the total charges on atoms k and l , ϵ is the local dielectric constant, R_{kl} is the distance between atoms k and l , C_{ra} is the coefficient of atomic orbital a in molecular orbital r , where r refers to the molecular orbitals on one molecule and s refers to those on the other, and E_r is the energy of molecular orbital r .

Radicals are very soft entities. The frontier orbital of these molecules is singly occupied (SOMO). The application of the Fukui–Klopman–Salem (FKS) method of perturbative molecular orbital theory (PMO) to a radical process is well established and it points out that the process is mainly controlled by the interaction between frontier orbitals, the charge term taking a secondary role. Therefore, the FKS equation can be simplified by grouping the first term, the endoergic term (due to overlapping between filled orbitals), and the second term or the Coulombic term due to the presence of point charges in the molecule. Then the equation takes the form

$$\Delta E = \Delta E_a + \sum_r \sum_s^{\text{occ}} \sum_s^{\text{unocc}} - \sum_s^{\text{occ}} \sum_r^{\text{unocc}} \frac{2(\sum_{ab} c_{ra} c_{sb} \beta_{ab})^2}{E_r - E_s} \quad (9)$$

As the radicals studied here are of the same nature, it has been assumed that the resonance integral β is the same when these radicals attack a given molecule. A second assumption is that the frontier orbitals which will determine the reactivity are the HOMO and LUMO in the unsaturated molecule and the SOMO in the radical. Then the FKS equation can be expressed as follows:

$$\Delta E = \Delta E_a + k c_{\text{SOMO}}^2 \left(\frac{c_{\text{HOMO}}^2}{E_{\text{SOMO}} - E_{\text{HOMO}}} + \frac{c_{\text{LUMO}}^2}{E_{\text{LUMO}} - E_{\text{SOMO}}} \right) \quad (10)$$

Thus, the SOMO of the radical will be able to interact with both the HOMO and the LUMO of the molecules bearing the double bond. The value of the energy gap between both frontier orbital process (SOMO–LUMO or SOMO–HOMO) will determine which of them is the most important, and then which is the preferred interaction that determines the reaction pathway (Figure 4).

By analogy with ground state organic reactions, (a) radicals are called nucleophilic radicals and (b) radicals are called electrophilic radicals.

Table 4. Geometric Parameters of the Radicals

R	radical	distance (Å)		angle (deg)	π -bond order (N–C ₁)
		C ₁ –N	N–C _{Ar}	H ₁ –C ₁ –H ₂	
H	DMA	1.384	1.433	119.3	0.240
CH ₃	DMT	1.383	1.433	120.2	0.242
CN	DMABN	1.382	1.421	120.3	0.250
CO ₂ Me	DMAMB	1.381	1.422	119.6	0.250
COPh	DMAB	1.382	1.425	119.7	0.250
COC ₆ H ₄ iPr	DMAIB	1.381	1.427	120.3	0.249

The purposes of the present quantum calculations can be summarized as follows: (1) to consider the effect of the substituent attached on the para position with respect to the dimethylamino group on the geometry and electronic structure of the radical, and (2) to examine the reactivity in the addition of several (dimethylamino)-phenyl radicals to butyl acrylate (BA) by applying a simple perturbative molecular orbital (PMO) model to these systems, which can be used to determine the interaction taking place.

(b1) Structural Parameters of Radicals. The calculated geometrical parameters of these radicals are depicted in Table 4.

The bond distance between the radical carbon and the nitrogen (C₁–N) is determined by the electronic effects (π -conjugation or polar effects) between them and, hence, will account for the effects of the R substituent on that particular carbon radical. As can be seen, there is an important shortening of this bond distance in comparison to the bond distance C₂–N (normally about 1.48 Å). This shortening has a direct correspondence with the electronic features of the group attached in the para position. Thus, taking as reference the radical of *N,N*-dimethylaniline, the bond distance shortens when the R substituent is electron withdrawing. The π -bond order existing between the carbon radical and the nitrogen was also calculated. As shown in Table 4 the values of these π -bond orders range from 0.25 to 0.24. As a π -bond order of 0.25 normally brings a shortening of 0.04 Å to the normal atom–atom distance, the observed bond shortening of about 0.09 Å should be attributed not only to the overlapping of Pz orbitals but also to charge effects.

An analogous correlation occurs with the bond distance between the C_{Ar} and the N (N–C_{Ar}). The stronger the electron-attracting behavior of R, the shorter is the N–C_{Ar} distance. It seems evident that the main factor of this geometrical parameter is merely due to resonance between the nitrogen and the aromatic ring.

(b2) Reactivity of Radicals. The theoretical study was done considering the attack of the dimethylamino radicals on butyl acrylate (BA). The HOMO energy of BA is –11.06 eV and its LUMO energy is –0.11 eV.

As shown in Table 5, the HOMO coefficients on carbons 1 and 2 are very similar. However, regarding the LUMO coefficients, the largest value is on carbon 1. To establish which position is more reactive, the reaction enthalpies of the attack of DMA radical on positions C₁ and C₂ of butyl acrylate were calculated. The values obtained are $\Delta H(\text{C}_1) = -15.05$ kcal/mol and $\Delta H(\text{C}_2) = -13.16$ kcal/mol. Therefore, as the control of the radical processes is mainly thermodynamic, the

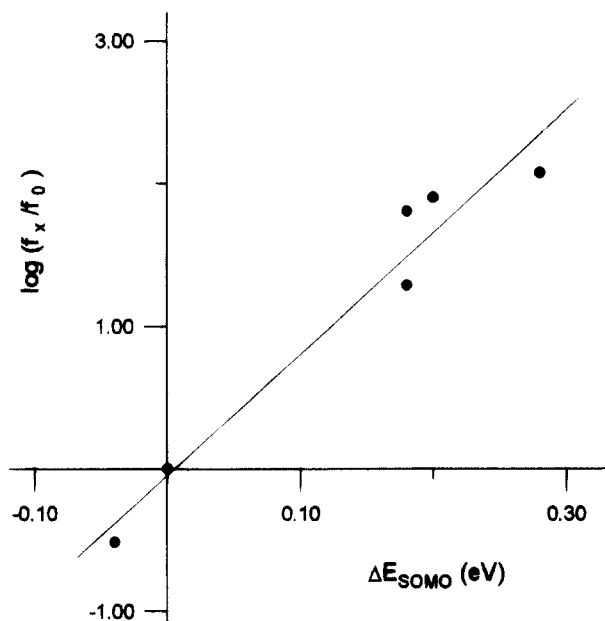
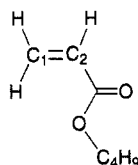


Figure 5. Plot of relative reactivity [$\log(f_x/f_0)$] vs SOMO energy.

Table 5. Electronic Parameters of Butyl Acrylate (BA)



carbon	charge	HOMO coeff	LUMO coeff
C ₁	-0.065	0.648	0.652
C ₂	-0.176	0.664	0.497

attack position for olefins with electron-withdrawing groups (as acrylates are) will be the less hindered (C₁). This result agrees with those obtained experimentally and published elsewhere.²³

In Table 6 are shown the electronic parameters (electronic density on radical carbon, SOMO energy, and orbital coefficient of the SOMO on the radical center) of the different radicals, the energy gap between the SOMO of the radical and the HOMO of BA ($\Delta E_{\text{SOMO-HOMO}}$), and the energy gap between the LUMO of BA and the SOMO of the radical ($\Delta E_{\text{LUMO-SOMO}}$). As can be observed, the lowest values of these gaps correspond to the SOMO-HOMO interaction, ca. 3.5 eV versus ca. 7.5 eV coming from the SOMO-LUMO interaction. Furthermore, the SOMO coefficients in the radical carbons are almost the same. Therefore, we can consider that the process will mainly depend on the first orbital interaction (SOMO-HOMO). Likewise, the electronic density values are practically identical in all of the radicals, and hence, the Coulombic interaction between BA and the different radicals will be almost constant. This fact led us to consider that the inclusion of the charge term on the endoergic term is correct.

The value of the SOMO energy could be related to an experimental measurement of the reactivity of these radicals, such as the efficiency factor ($\log(f/f_0)$) (Figure 5). In trying to make the representation as similar to that of the Hammett parameter as possible, E_{SOMO} values have been taken as relative, making the origin of the axis the value for the HDMA derivative and then representing $\log(f_x/f_0)$ vs ΔE_{SOMO} [being $\Delta E_{\text{SOMO}} = E_{\text{SOMO}}(\text{xDMA}) - E_{\text{SOMO}}(\text{HDMA})$].

Table 6. Electronic Parameters of the Radicals

radical	electronic density on C ₁	SOMO energy (eV)	SOMO coeff on C ₁	$\Delta E_{\text{SOMO-HOMO}}$ (eV)	$\Delta E_{\text{LUMO-SOMO}}$ (eV)
DMA	-0.417	-7.62	0.62	3.45	7.51
DMT	-0.419	-7.58	0.61	3.49	7.47
DMABN	-0.412	-7.94	0.62	3.17	7.79
DMAMB	-0.415	-7.80	0.61	3.27	7.69
DMAB	-0.411	-7.82	0.62	3.25	7.71
DMAIB	-0.413	-7.80	0.62	3.27	7.69

As can be seen in Figure 5, the plot is linear with a good correlation coefficient, and again the line of best fit passes through (0,0); the experimental values in the diagram show a behavior almost identical to that in Figure 3. Therefore, the calculated reactivity order, considering that the radical addition of the initiator is controlled by the SOMO energy, totally agrees with the experimental one. This order is as follows:



Conclusions

Good correlation has been found between the efficiencies of the radicals arising from the *N,N*-dimethylaniline derivatives studied and the empirical factor σ_p present in the Hammett equation. The same relationship has been found between the efficiencies and the SOMO energy of the mentioned radicals, which indicates that the reactivity increases as the electron-withdrawing character of the substituent in the para position increases.

Thus, it seems that the simple perturbative molecular orbital calculations (PMO) could be used to determine the relative radical reactivities in the reaction of initiation of radical polymerization.

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