PII: S0032-3861(96)00934-2

A molecular orbital study of the dimerization process of acrylic monomers

M. A. Mora*
Departamento de Química, Universidad Autónoma Metropolitana, Campus Iztapalapa, Mexico, D. F., CP. 09300

and M. Rubio
Instituto de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, Circuito Exterior, CP. 04510, México, D. F., México

Molecular orbital calculations have been carried out for dimerization steps in the polymerization process of methyl acrylate, methyl methacrylate, and ethyl acrylate through free radicals and ionic mechanisms. The calculations were performed for monomers, dimers, their positive and negative ions, and free radicals. The minimum energy geometry was achieved in all cases, the geometrical and electronic parameters are analysed, a dimerization reaction pathway is proposed, the heats of polymerization obtained are in excellent agreement with experimental data. © 1997 Elsevier Science Ltd.

(Keywords: acrylic monomers; molecular orbital calculations; heats of polymerization)

INTRODUCTION

The intramolecular polymer structure (sequence distribution and tacticity) is important, because it may supply information about the monomer addition process, e.g. about the preference of monomers to add in the iso- or syndiotactic configuration[1,2]. Moreover, knowledge about the intramolecular structure is of paramount importance for the understanding of relations between structure and polymer properties[3] and there is significant interest in characterizing polymeric materials (especially blends) at the molecular level. This interest is due, in part, to the tremendous technological importance of polymer blends. The bulk, macroscopic properties of such materials are determined by the microscopic structure that, in turn, is critically dependent on the degree of molecular mixing between blend components. The special properties of polymer materials arise from differences between the thermodynamic interactions in systems containing macromolecules and those systems of only small molecules.

The nature of intermolecular interactions determines the microscopic structure in any condensed-phase system. However, when the system contains macromolecules there is additional complexity due to intramolecular considerations; the number of configurations available to a polymer chain, although restricted by covalent bond geometries, is vast. Thus, the morphology of a chain involves the interplay between the interactions of the polymer with its environment and the possible chain conformations. To understand these systems more fully, it is desirable to investigate quantitatively the interactions of isolated polymer chain.

In this paper, the results of semi-empirical molecular orbital calculations for monomers, dimers, their positive and negative ions and free radicals participating in the dimerization step in the polymerization process of methyl acrylate (MA), methyl methacrylate (MMA), and ethyl acrylate (EA) by free radicals and ionic mechanisms are presented. Using the AM1 (Austin Model 1) hamiltonian proposed by Dewar and co-workers[4] we have optimized the geometry of the above systems. Also, we have examined the evolution of the conformations and the bonding when a monomer unit is approached to a monomeric specie (ion or free radical). In other words we have explored a reaction coordinate.

The AM1 method embodies the approximations that are inherent to the neglect of diatomic differential overlap (NDDO) formalism[5], and overcome the major weakness of the MNDO (modified neglect of differential overlap) method[6,7] in which it is based. It is known that the AM1 method produce fairly accurate equilibrium geometries, orbital orderings, and partial charges[8]. Geometry optimizations could be carried out using the AM1 hamiltonian without unduly high computer and memory requirements.

METHODOLOGY

Minimum energy conformations for methyl acrylate, methyl methacrylate, and ethyl acrylate monomers were obtained in previous work[9]. Based on those geometries, the corresponding model compounds of dimers were formed, in each case the initial geometry corresponds to an isotactic all-*trans* conformation.

With these geometries an optimization process was initiated, in a first step full optimization calculations were made for each dimer, and with these new

---

* To whom correspondence should be addressed

geometries, rotational barriers were calculated taking for rotation axes the C–C skeletal bonds flanking carbon C7 (see *Figure 1*), the torsion angles were changed with increments of 20° in each particular case, in each point all the non-hydrogen geometrical parameters were varied simultaneously.

For the dimer models formed in this way, one hydrogen atom was removed to form free radicals, and, by assigning a positive or negative charge to the system
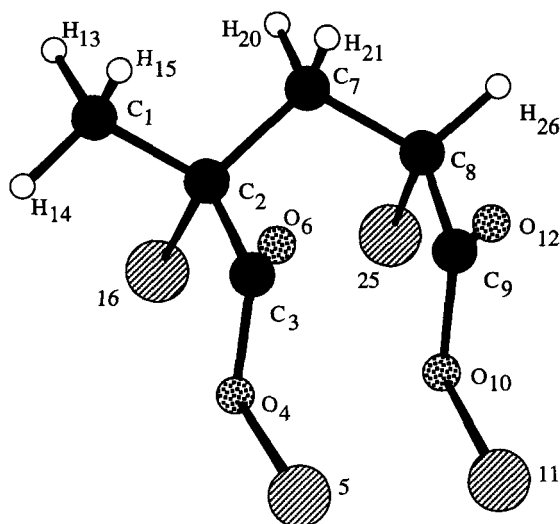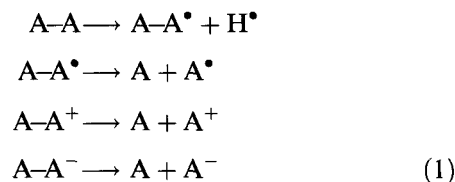

Figure 1 Schematic representation of acrylic dimers, groups 16 and 25 = –H or –CH₃; groups 5 and 11 = –CH₃ or –C₂H₅

the corresponding cations and anions were formed. These processes were made with optimization of the geometrical parameters for the atoms nearest to the site where the hydrogen atom was removed. The next step was to break the bond between monomeric units, it was done changing in steps of 0.2 Å the C2–C7 bond distance from the equilibrium distances to 7 Å, for this step two calculations were made, in the first the geometrical parameters of the atoms nearest to the bond breaking site were optimized, in the second one all the geometrical parameters were optimized, except the C7, C8, C9 bond angles and the O10 dihedral angle to prevent the formation of compounds different to that required. A schematic view of the process is:

$$A\text{–}A \longrightarrow A\text{–}A^\bullet + H^\bullet$$

$$A\text{–}A^\bullet \longrightarrow A + A^\bullet$$

$$A\text{–}A^+ \longrightarrow A + A^+$$

$$A\text{–}A^- \longrightarrow A + A^- \tag{1}$$

Where A–A represents a dimer molecule formed by two monomers of A, A–A$^\bullet$ is the free radical of the dimer, A–A$^+$ is a cationic dimer and A–A$^-$ is an anionic dimer.

The minimum energy conformation of the different monomeric and dimeric species was calculated. The bond dissociation energy is the difference between the sum of the calculated total energies for the right side species in its minimum energy conformation and the total energy of the left side compound also in its
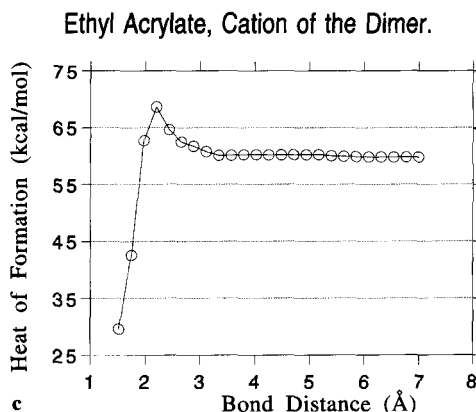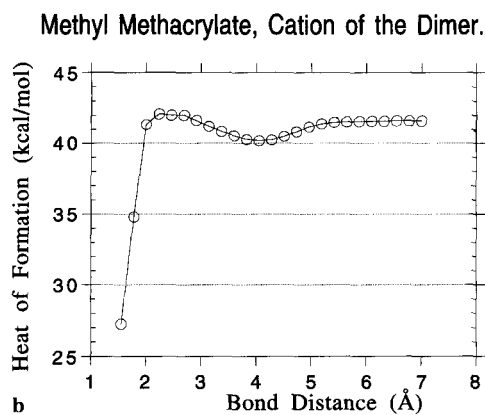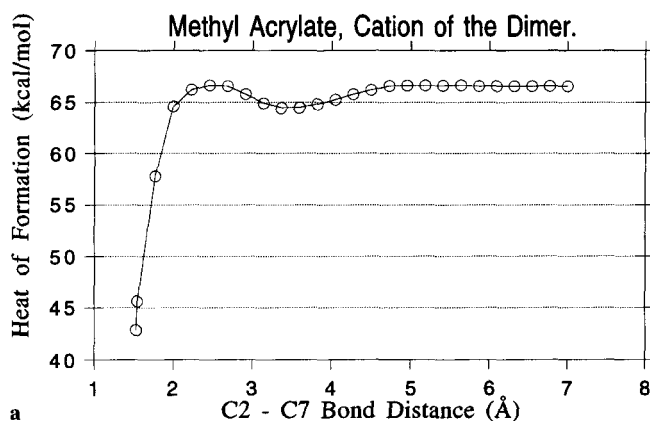

Figure 2 The heat of formation vs the C2–C7 bond distance for (a) methyl acrylate dimer cation; (b) methyl methacrylate dimer cation; (c) ethyl acrylate dimer cation

minimum energy conformation. The minimum-energy geometry and total energy for each of the radicals, cations and anions were found by allowing all atoms to move.

The potential energy curves for the dimer cations dissociation (the third process in equation (1)) are shown in *Figure 2*. The heat of dissociation this way obtained must be the negative of the polymerization heat in terms of monomer unit added.

RESULTS AND DISCUSSION

Methyl acrylate

In a previous work[9] we reported the minimum energy conformation for the methyl acrylate monomer, using that geometry the methyl acrylate dimer was formed. The model compound used in this work to represent the MA-dimer corresponds to methyl groups in positions 5 and 11, and hydrogens in positions 16 and 25 (*Figure 1*). The various atoms are numbered and will hereafter be referred to by these numbers, this dimer has an isotactic all-*trans* conformation. For this geometry, a calculation with full optimization (all the geometric parameters were varied simultaneously) was made, with this new geometry and taking the bond C7–C8 as axis of rotation, the

rotational barrier was calculated from $0°$ to $360°$ with angle increments of $20°$; $0°$ corresponds to having the bond C8–C9 *cis* to the bond C2–C7, at each point the position of the ester groups atoms were optimized. From this rotational barrier the minimum energy conformation was taken as initial for the next rotational barrier calculation through the bond C2–C7, optimization of the geometrical parameters for the atoms neighbouring this bond was made again, and using the new minimum energy conformation a full optimization calculation was carried out. In *Table 1* the most relevant geometrical parameters are shown. By adopting the convention given by Flory and co-workers[10]. The final geometry corresponds to a t_g conformation. *Figure 3* shows the final conformation in the form of Newman diagrams.

With the minimum energy conformation for the dimer obtained in this way, the bond distance C8–H26 was changed with increments of $0.2\,\text{Å}$ from the equilibrium value to $5\,\text{Å}$, this bond enlargement is equivalent to the dimer dissociation in one hydrogen and one dimer free radicals. The dissociation process was made with optimization of the geometrical parameters for the atoms nearest to the bond being broken. Here it should be noticed that the bond values of the angles C7–C8–C9 and C7–C8–H25 change from almost tetrahedral in the initial conformation (110.85 for C9, see *Table 1*) to

Table 1 Relevant geometrical features for the dimer of methyl acrylate

	RA	Bond length (Å)	RA	Bond angle (deg.)	RA	Torsional angle (deg.)
C2	C1	1.516				
O3	C2	1.507	C1	109.016		
O4	C3	1.368	C2	112.746	C1	−108.245
C5	O4	1.428	C3	116.831	C2	178.898
O6	C3	1.232	C2	129.140	C1	71.425
C7	C2	1.521	C1	110.598	C3	121.204
C8	C7	1.514	C2	111.547	C1	170.140
C9	C8	1.496	C8	110.855	C2	−172.693
O10	C9	1.369	C2	112.683	C7	−148.868
C11	O10	1.428	C9	116.773	C8	−179.091
O12	C9	1.232	C8	129.134	C7	32.229
H20	C7	1.123	C2	109.069	C1	49.143
H21	C7	1.123	C2	109.366	C1	−68.247
H25	C8	1.124	C7	110.669	C2	−53.715
H26	C8	1.123	C7	110.452	C2	65.560

The reference atom (RA) is the atom with respect to which the bond length, bond angle or dihedral angle is measured

Table 2 Some relevant geometrical parameters of the methyl acrylate cation of the dimer

	RA	Bond length (Å)	RA	Bond angle (deg.)	RA	Torsional angle (deg.)
C2	C1	1.515				
C3	C2	1.507	C1	109.768		
O4	C3	1.363	C2	110.986	C1	−121.552
C5	O4	1.435	C3	117.075	C2	173.831
O6	C3	1.229	C2	130.343	C1	59.472
C7	C2	1.543	C1	109.567	C3	121.041
C8	C7	1.418	C2	115.973	C1	169.451
C9	C8	1.492	C7	120.101	C2	−171.650
O10	C9	1.349	C8	112.390	C7	−143.799
C11	O10	1.444	C9	99.933	C8	179.610
O12	C9	1.229	C8	124.741	C7	37.061
H20	C7	1.156	C8	108.847	C9	−67.088
H21	C7	1.149	C8	110.945	C9	42.281
H25	C8	1.115	C7	122.382	C9	7.077

The reference atom (RA) is the atom with respect to which the bond length, bond angle or dihedral angle is measured
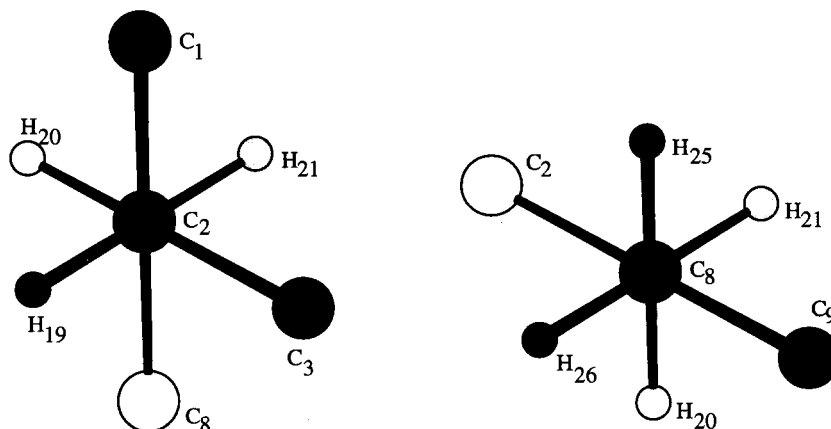

Figure 3 Newman diagrams for the methyl acrylate dimer in its lowest energy conformation
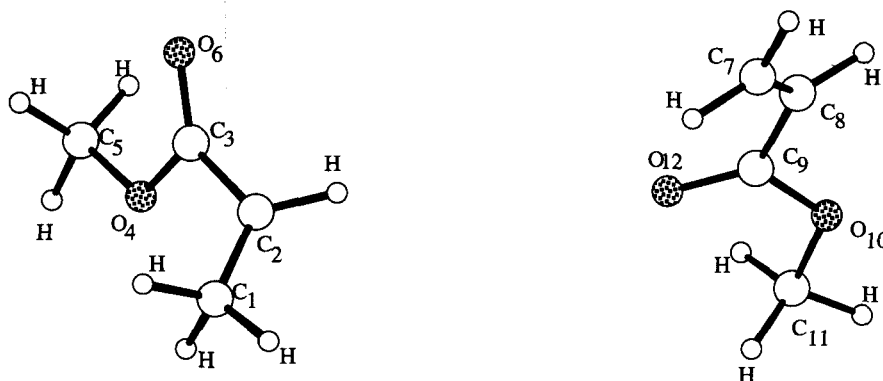
Figure 4 Dissociation products of the methyl acrylate cationic dimer

Table 3 Net atomic charges for the different dimer species of methyl acrylate

Atom	Dimer		
	Neutral	Cation	Dissociated Cation
C1	−0.211	−0.228	−0.340
C2	−0.095	−0.101	0.340
C3	0.297	0.269	0.233
O4	−0.280	−0.280	−0.274
C5	−0.065	−0.068	−0.064
O6	−0.347	−0.305	−0.196
C7	−0.157	−0.281	−0.147
C8	−0.160	0.315	−0.174
C9	0.302	0.237	0.333
O10	−0.278	−0.231	−0.260
C11	−0.064	−0.067	−0.064
O12	−0.352	−0.229	−0.384
H13	0.085	0.093	0.130
H14	0.102	0.127	0.190
H15	0.085	0.108	0.280
H16	0.120	0.140	0.220
H17	0.087	0.131	0.120
H18	0.089	0.103	0.120
H19	0.121	0.130	0.140
H20	0.110	0.320	0.140
H21	0.115	0.250	0.114
H22	0.084	0.150	0.115
H23	0.090	0.120	0.173
H24	0.120	0.118	0.086
H25	0.100	0.220	0.080
H26	0.120		

Table 4 Some relevant geometrical parameters of the dissociated cation of the methyl acrylate dimer

	RA	Bond length (Å)	RA	Bond angle (deg.)	RA	Torsional angle (deg.)
C2	C1	1.415				
C3	C2	1.488	C1	120.991		
O4	C3	1.363	C2	109.028	C1	−53.508
C5	O4	1.442	C3	116.774	C2	−175.164
O6	C3	1.223	C2	130.345	C1	127.087
C7	C2	7.0	C1	128.268	C3	−170.031
C8	C7	1.332	C2	115.973	C1	101.186
C9	C8	1.471	C7	120.823	C2	−24.303
O10	C9	1.365	C8	113.262	C7	−144.872
C11	O10	1.429	C9	116.888	C8	−177.935
O12	C9	1.237	C8	128.403	C7	37.061
H20	C7	1.099	C2	121.892	C1	1.312
H21	C7	1.099	C2	122.564	C1	−178.758
H25	C8	1.102	C7	123.814	C2	−178.758
H26	C8					

The reference atom (RA) is the atom with respect to which the bond length, bond angle or dihedral angle is measured

almost trigonal values when the system is dissociated (120.1 for C9, see *Table 2*), and the atomic electronic densities for the atoms neighbouring C7 are substantially changed (*Table 3*). With the dimer free radical geometry this way obtained and the program parameter charge made equal to zero, one or minus one, the geometries and heats of formation were obtained for the free radical, cation and anion dimeric species respectively.

For each of these three species the C2–C7 bond distance was changed from the equilibrium value to 7 Å with increments of 0.2 Å (25 calculations), the potential energy curve for the dimer cation dissociation in the corresponding neutral and cation monomers is shown in *Figure 2a*, it can be seen that around the 2.5 Å distance the energy is a maximum, which means that the dimer cation is dissociated and the C2–C7 bond is almost broken, however in the 2.5–5 Å range some attractive interactions occur between O12 and C2. *Table 4* shows some relevant geometrical parameters obtained for the dimer cation dissociated, notice the geometry adopted by the monomeric species. *Table 3* shows the net atomic charges on each atom for the dimer cation and the dissociated dimer cation, the sign and magnitude of the charges on the atoms C2, C7 and C8 should be noticed. C2 has a positive net atomic charge because when the C2–C7 bond is broken a monomeric cation with an electron deficient carbon atom is formed, the cationic character is on C2. On the other hand, the other dissociation product is a monomer unit with a C7–C8 double bond, this double bond is evident from the net atomic charges on the C7 and C8 atoms which both have negative values. Some relevant geometrical parameters
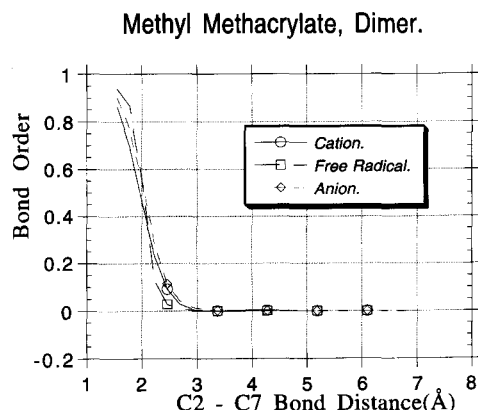

Figure 5 C2–C7 bond distance vs bond order energy from the dissociation step of the methyl methacrylate ions and free radical

for the cation of the methyl acrylate dimer and the methyl acrylate dissociated cation of the dimer are shown in *Tables 2* and *4*, respectively, notice the monomer geometry which is planar and the non planar geometry for the monomer cation. *Figure 4* shows the geometry adopted by the dissociation products.

For the free radical and anion dimers, similar processes were carried out for the optimization and bonds enlargement steps in order to obtain the corresponding dissociation energies and monomeric geometries.

By reversing the process direction we obtain the dimerization process (propagation step in a polymerization mechanism). The heats of polymerization calculated for MA are, $-24.62 \, \text{kcal mol}^{-1}$ for the cationic mechanism, $-24.04 \, \text{kcal mol}^{-1}$ for the free radicals mechanism and $-31.29 \, \text{kcal mol}^{-1}$ for the anionic mechanism; the experimental value from the literature[11,12] is $-18.8 \, \text{kcal mol}^{-1}$.

Methyl methacrylate

Figure 5 shows the curves of the C2–C7 bond distance vs bond order energy for the dissociation of the three species of methyl methacrylate, there, the bond order is approximately zero at a distance of 3 Å for the cationic and anionic species but not for the free radical which has an almost null bond order value before 3 Å, the bond breaking is sudden, this fact is shown by the corresponding curve slope. For the cationic species, when the C2–C7 bond distance is increased it is broken forming a methyl methacrylate monomer with a C7–C8 bond and a

monomer cation. The cationic character of the dimer is appreciated by the net atomic charge on C8 atom (see *Figure 6*), this charge changes sign at approximately 2.5 Å, the charge on C7 is more negative between 1.5 and 2.5 Å. Once the C2–C7 bond is broken there is a readjustment in the monomer charges resulting in the C7 and C8 atoms having almost the same negative charge (long distances in *Figure 6*). The other dissociation fragment is a monomer with cationic character on the C2 atom, this atom has a small negative charge at the equilibrium distance but when the bond distance is increased to 2.5 Å the charge is positive, showing the cationic character of this fragment, the change in charge on the C1 atom is small.

When the C2–C7 bond is breaking there is a change in the bond and dihedral angles of the atoms bonded to C2, this is because a hybridization occurs on C2 from sp_3 in which the bond orientation is almost tetrahedral to sp_2 with a triangular bond arrangement, this last fact is better appreciated in *Figure 7*, there the C3 and C16 bond angles change from near tetrahedral values (108.9° for C3 and 110.97° for C16) to triangular angles (near 120°). The change in the C8 bond angle from 112° to almost 90° shows the trajectory followed by the monomer cation when it is approaching the molecular monomer.

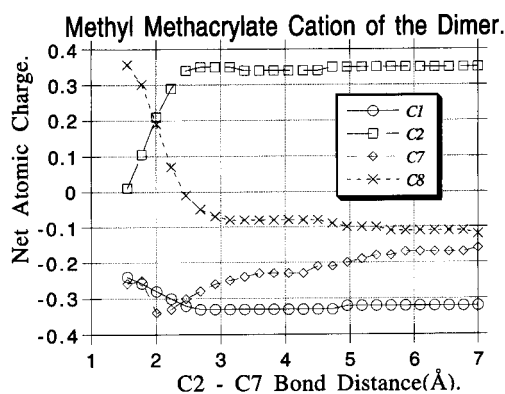*Figure 8* presents the dihedral angle variation vs the C2–C7 bond distance for the MMA–cationic dimer,

Figure 8 Dihedral angles vs the C2–C7 bond distance for the dissociation of methyl methacrylate cation of the dimer

Figure 6 Net atomic charge on the main chain atoms vs the C2–C7 bond distance for the dissociation of methyl methacrylate cation of the dimer
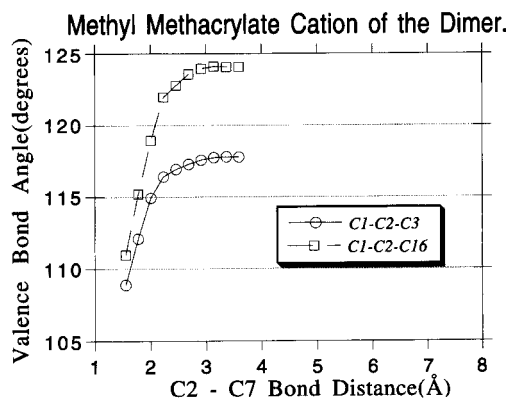

Figure 7 C3 and C8 bond angles vs the C2–C7 bond distance for the dissociation of methyl methacrylate cation of the dimer
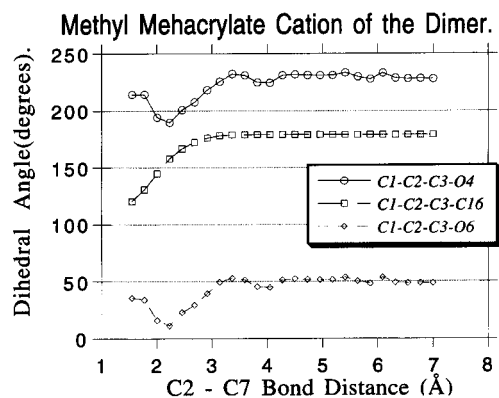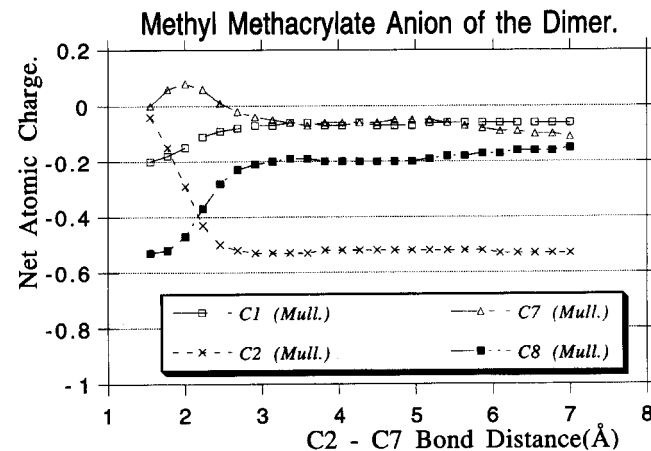

Figure 9 Net atomic charges on the main chain atoms vs the C2–C7 bond distance for the dissociation of methyl methacrylate anion of the dimer

there, the acrylic group orientation is modified by almost $-30°$ between the equilibrium distance and 2.3 Å, after that distance a new orientation change occurs (this time about $60°$), finally the acrylic group orientation is $48.5°$ out of the C1–C2–C3 plane for the cationic monomer formed. The curve for the C16 atom shows how the dihedral angle is changing from a tetrahedral value (approximately $120°$) to a trigonal one (near to $180°$). Again this fact shows a change in the hybridization on the C2 atom.

The dissociation products of the MMA anion of the dimer are an anion monomer and a molecular monomer, from the net atomic charge variation vs the C2–C7 bond distance (*Figure 9*) is appreciated how is changing anionic character of the dimer with the C2–C7 bond distance, the net atomic charge on C8 goes from -0.5 at the equilibrium distance value to around -0.2 for distances greater than 3 Å, on the other hand, the net atomic charge on C2 goes from almost zero to -0.55, this
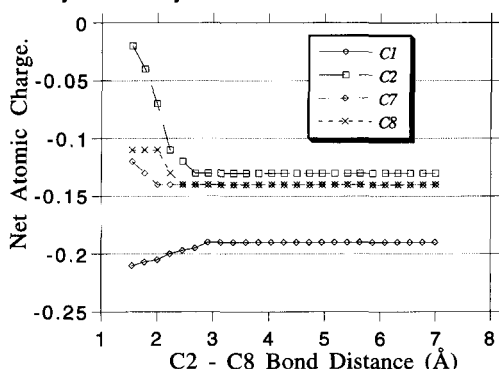

Figure 10 Net atomic charges on the main chain atoms vs the C2–C7 bond distance for the dissociation of methyl methacrylate free radical of the dimer

fact confirms that in this case again the dissociation occurs giving the above products.

For the MMA-free radical dimer the net atomic charges vs the C2–C7 bond distance curves are presented in *Figure 10*. It is appreciated that the charges on the principal skeletal atoms are without a change in sign, the charges are only redistributed. The energy difference between products and reactants (see equation (1)) is a measure of the polymerization heat, the calculated values for methyl methacrylate are: -13.91, -25.05 and $-16.39 \text{ kcal mol}^{-1}$ calculated for the cationic, anionic and free radical mechanism, respectively, the value calculated for the cationic species are in excellent agreement with the experimental value: $-13.5 \text{ kcal mol}^{-1}$ [13].

Ethyl acrylate

In the dimer initial conformation, the substituent groups were oriented in a parallel position, from this conformation, rotational barriers were calculated, the first of these was obtained turning through the C7–C8 bond with increments of $20°$ and simultaneous coordinates variation for each point, in addition the rotational barriers through the C2–C7 and C8–C9 bonds were calculated. The final conformation for the EA–neutral dimer is shown in *Figure 11*. With the minimum energy conformation obtained in this way, and, to obtain a dimer free radical the C8–H26 bond distance was changed from 1.125 to 5.0 Å with increments of 0.3 Å. The heat of formation variation vs the C8–H26 bond distance is shown in *Figure 12*, the bond distance value for the formation of EA–free radical is about 3 Å. When this bond distance is changing, the C9 bond and dihedral angles go from tetrahedral ($110.68°$, $179.78°$) to trigonal ($118.16°$, $59.8°$) values. Similar changes occur with the H25 position which changes from $111.08°$ and $-57.6°$ to $119.97°$ and $-121.9°$.

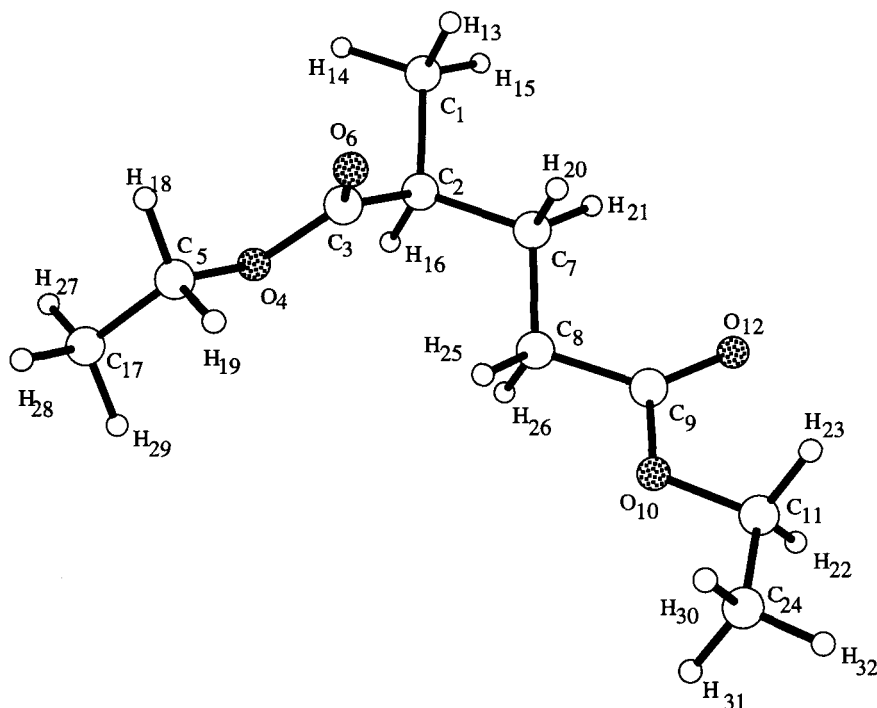With this geometry and placing a $+1$ or -1 charge on the compound, the EA–cationic or EA–anionic dimeric

Figure 11 Ethyl acrylate dimer lowest energy conformation

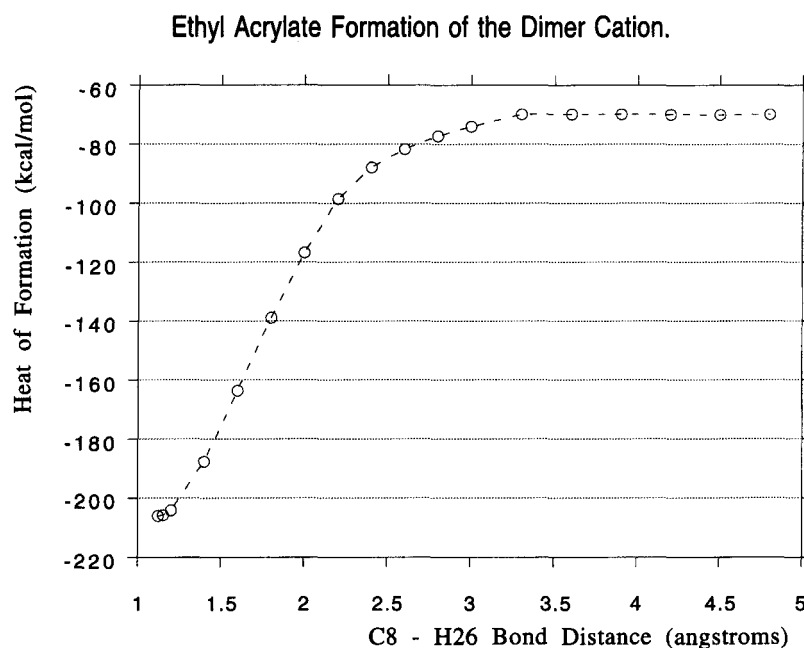## Ethyl Acrylate Formation of the Dimer Cation.

Figure 12 C8–H26 bond distance vs the heat of formation for the ethyl acrylate free radical of the dimer

species were modelled, for every one of the three dimeric species (cation, anion and free radical) the C2–C7 bond distance was changed to obtain the heat of dissociation, this heat of dissociation with the sign changed must be the heat of formation of the EA dimeric species, this bond distance was changed from the equilibrium value to 7 Å with full optimization in each point, the dissociation products are a molecular monomer and a monomeric species. In the final geometry adopted by these products it is possible to appreciate the hybridization on the C2 and C7 atoms, tetrahedral in the dimeric species and trigonal when dissociated (*Figure 13* shows the final geometry adopted by the fragments resulting from the cleavage of the C2–C7 bond in the case of the cation of the EA dimer), on the C2 atom not only a change of hybridization occurred, but also a change in charge going from −0.09 in the neutral dimer to −0.11 in the cation of the dimer and to +0.38 when the dissociation product is a cation of the monomer.

Table 5 shows the net atomic charges on the atoms for the different EA dimeric species. The C8 net atomic charge changes in such a way that reflects the character of the different EA dimeric species.

The heat of polymerization calculated for the ethyl acrylate by way of the cationic mechanism is −28.08 kcal mol^{-1}, the values calculated by the anionic and free radical mechanisms are −21.58 and −22.86 kcal mol^{-1}, respectively. The experimental value is −18.8 kcal mol^{-1} [14].

CONCLUSIONS

We have optimized the geometry of monomers and dimers in their neutral, cationic, anionic and free radical forms. The polymerization heats obtained from the dissociation process are in good agreement with the literature. With the methods used in this work it is possible to appreciate the rearrangement of the
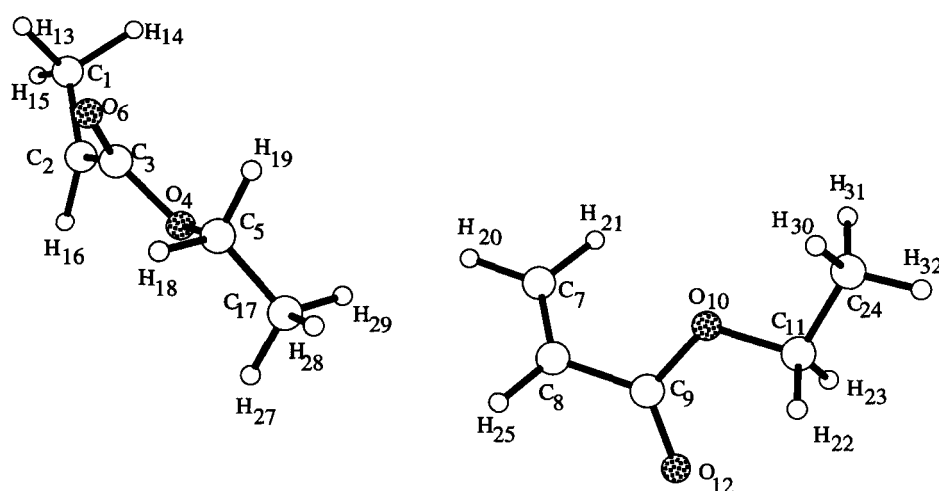

Figure 13 Dissociation products of the ethyl acrylate cation of the dimer

Table 5 Atomic charge from electrostatic potentials for the ethyl acrylate dimeric species

Atom	Neutral	Cation	D.C.[a]	Anion	F.R.[b]
C1	-0.233	-0.172	-0.270	-0.109	-0.198
C2	-0.255	-0.199	0.444	-0.369	-0.246
C3	0.889	0.686	0.598	0.887	0.841
O4	-0.538	-0.449	-0.409	-0.541	-0.513
C5	0.208	0.115	0.171	0.239	0.194
O6	-0.576	-0.465	-0.426	-0.587	-0.561
C7	0.150	-0.091	-0.039	0.451	0.184
C8	-0.565	0.360	-0.400	-1.221	-0.480
C9	0.895	0.652	0.859	0.935	0.886
O10	-0.505	-0.452	-0.483	-0.507	-0.490
C11	0.176	0.140	0.193	0.159	0.155
O12	-0.575	-0.422	-0.539	-0.717	-0.562
H13	0.080	0.100	0.240	0.030	0.070
H14	0.080	0.081	0.190	0.051	0.071
H15	0.100	0.076	0.130	0.051	0.080
H16	0.110	0.120	0.120	0.130	0.103
C17	-0.234	-0.237	-0.253	-0.219	-0.241
H18	0.040	0.081	0.080	0.010	0.040
H19	0.040	0.080	0.080	0.032	0.040
H20	0.040	0.180	0.090	-0.050	0.040
H21	0.020	0.180	0.030	-0.040	0.040
H22	0.050	0.084	0.056	0.027	0.056
H23	0.050	0.091	0.051	0.013	0.055
C24	-0.243	-0.215	-0.277	-0.187	-0.237
H25	0.160	0.130	0.190	0.220	0.180
H26	0.016				
H27	0.087	0.078	0.092	0.099	0.087
H28	0.062	0.101	0.109	0.029	0.065
H29	0.084	0.081	0.094	0.066	0.086
H30	0.089	0.094	0.095	0.067	0.091
H31	0.089	0.088	0.095	0.066	0.084
H32	0.067	0.092	0.089	0.017	0.066

[a] Cation of the dissociated dimer
[b] Free radical of the dimer

electronic densities on the atoms. In all the cases where a bond rupture or a bond formation (ionization and dimerization) occurred were observed changes in the hybridization of the atoms directly involved in such a process.

From the energy differences for the process of dimerization it is possible to see that for the ethyl acrylate the anionic mechanism seems to be the most possible, followed by the free radical. The more-favoured mechanism for methyl acrylate is free radicals followed by the cationic. For methyl methacrylate the minimum energy calculated corresponds to the cationic followed by the free radicals mechanism. This order of polymerization is in excellent agreement with the Schildknecht classification[15].

Many possibilities may be suggested for the path followed by the monomers in their approach to each other, but only one path is possible in the dissociation process, this path is what we are proposing for the dimerization path for MMA, MA, and EA.

REFERENCES

1. Koening, J. L., *Chemical Microstructure of Polymer Chains*. Wiley, New York, 1980.
2. Frish, H. L., Mallows, G. L., Hestley, F. and Bovey, F. A., *Macromolecules*, 1968, **1**, 553.
3. Pichot, C. H., Llauro, M. and Pham, Q., *J. Polym. Sci., Polym. Chem. Ed.*, 1981, **19**, 2619.
4. Dewar, M. J. S., Zoeblisch, E. G., Ealy, E. F. and Stewart, J. J. P., *J. Am. Chem. Soc.*, 1985, **107**, 3902.
5. Dewar, M. J. S., *The Molecular Orbital Theory of Organic Chemistry*. McGraw-Hill, New York, 1969.
6. Dewar, M. J. S. and Thiel, W., *J. Am. Chem. Soc.*, 1977, **99**, 4899, 4907.
7. Stewart, J. J. P., Dewar, M. J. S., MOPAC 4.0, QCPE #455, Blomington In., 1987.
8. Dewar, M. J. S. and Storch, D. M., *J. Am. Chem. Soc.*, 1985, **107**, 3898.
9. Mora, M. A., Rubio, M. and Salcedo, R., *Polymer*, 1993, **34**, 5143.
10. Flory, P. J., Sundararajan, P. R. and DeBolt, L. C. *J. Am. Chem. Soc.*, 1974, **96**, 5015.
11. Rodriquez, F., *Principles of Polymer Systems*. McGraw-Hill, New York, 1982.
12. Flory, P. J., *Principles of Polymer Chemistry*. Cornell University Press, Ithaca, 1978.
13. Joshy, R. M. and Zwolinski, B. J., in *Vinyl Polymerizations*, Vol. 1, ed. G. E. Ham, Marcel Dekker, New York, 1967.
14. Flory, P. J., *Principles of Polymer Chemistry*. Cornell University Press, Ithaca, 1978, p. 254.
15. Schildknecht, C. E., Gross, S. T., Davison, H. R., Lambert, J. M. and Zozz, A. O. *Ind. Eng. Chem.*, 1948, **40**, 2104.