

Free-Radical Homopolymerization and Copolymerization of Ethyl α -Hydroxymethylacrylate in Tetrahydrofuran

M. C. FERNÁNDEZ-MONREAL,¹ R. CUERVO,¹ and E. L. MADRUGA^{2*}

¹Departamento de Química Orgánica I, Facultad de C. Químicas, Universidad Complutense, 28040-Madrid, Spain,

²Instituto de Ciencia y Tecnología de Polímeros (CSIC), Juan de la Cierva, 3. 28006-Madrid, Spain

SYNOPSIS

Ethyl α -hydroxymethylacrylate (EHMA) was polymerized in a 3 mol/L tetrahydrofuran solution at 50°C, using 2-2' azobisisobutyronitrile as initiator. The kinetic behavior indicates a higher polymerization rate for EHMA than for methyl methacrylate (MMA). Copolymerization reaction between MMA and EHMA, under the same experimental conditions, was carried out and values of $r_{\text{MMA}} = 1.264$ and $r_{\text{EHMA}} = 1.285$ were found for the reactivity ratios. The comparison of triad sequences as determined from Bernoullian statistic to those calculated from the experimental splitting of *O*-methyl and α -methyl ¹H-NMR signals of the copolymers confirm the obtained results. © 1992 John Wiley & Sons, Inc.

Keywords: free radical polymerization • ethyl α -hydroxymethylacrylate • homopolymerization • copolymerization • copolymer structure

INTRODUCTION

In previous articles¹⁻⁵ we have reported studies on synthesis, free-radical homopolymerization, and copolymerization of several methyl α -benzylacrylates. These investigations revealed that:

1. Methyl α -benzylacrylates have apparent ceiling temperatures ranging between 65 and 100°C in a 5 mol/L benzene solution. On the other hand, rates of homopolymerization, determined by gravimetric measurements, and molecular weights of polymers are low in comparison to those of the methyl methacrylate.
2. The trends in copolymerization of methyl methacrylate with methyl α -benzylacrylates suggest a propagation-depropagation mechanism in which a large decrease in overall rate of copolymerization and in average molecular weight occurs as methyl α -benzylacrylates increase in the feed.

Alkyl α -(phenoxymethyl) methacrylates have also been polymerized with relatively low yields

and molecular weight.⁶ Other methyl aryloxymethacrylates have been also prepared by Balakrishnan et al.⁷

Methyl α -*n*-alkylacrylates have been prepared and successfully homopolymerized anionically, but attempts to initiate polymerization of these compounds with a radical initiator resulted in either low molecular weight polymer or no polymer at all.^{8,9}

As a part of the study of the α -methyl substituted methacrylates [$\text{CH}_2=\text{C}(\text{CH}_2\text{Z})-\text{COOR}$] behavior in polymerization we focused our attention on a functional acrylate monomer: ethyl α -hydroxymethylacrylate (EHMA). In fact, EHMA is a monomer which contains three different functionalities including an alcohol, an ester, and a polymerizable double bond. The hydroxyl group was expected to increase both the monomer hydrophilicity and the hydrogen bonding capability; in this way Mathias et al.¹⁰ have utilized EHMA alone or copolymerized with other monomers¹¹ to improve the mechanical properties of wood. Other possible applications as a new acrylate crosslinking agent have also been explored.¹²

Free-radical homopolymerization of EHMA in bulk and in ethyl acetate or ethanol solution, as well as the copolymerization with styrene in ethyl acetate have been carried out by Ueda et al.,¹³ and so has the copolymerization of EHMA with 2-vinyl-4,4'-dimethylazlactone.¹⁴ Other similar monomers such

* To whom all correspondence should be addressed.

as methyl α -hydroxymethylacrylate¹⁵ and α -hydroxymethylacrylonitrile¹⁶ have also been copolymerized with styrene.

In order to gain insight on the kinetic trend of α -methyl substituted methacrylates this article describes the free-radical homopolymerization of EHMA and its copolymerization with methyl methacrylate in tetrahydrofuran solution.

EXPERIMENTAL

2,2'-Azobisisobutyronitrile (AIBN) was purified by crystallization from methanol. Tetrahydrofuran (THF) HPLC grade (Scharlau) was distilled in the presence of potassium hydroxide; methyl methacrylate (MMA) was purified by conventional methods.¹⁷

The ethyl α -hydroxymethylacrylate was prepared according to the method reported by Villieras et al.¹⁸ with a slight modification. A saturated solution of potassium carbonate (48 g, 0.35 mol) was slowly added to a mixture of triethyl phosphonate (44.8 g, 0.2 mol.) and a 30–40% aqueous formaldehyde solution (86 mL); the mixture was stirred for 1 h at room temperature. Then, saturated ammonium chloride solution (75 mL) was added and the mixture was extracted with diethyl ether. The organic extracts were dried (MgSO_4) and evaporated. The crude oil was purified by flash chromatography on a silica gel column, eluting with ethyl acetate:hexane (20:80) to obtain 14.6 g (56%).

IR (neat, cm^{-1}): 3400 (OH); 1710 (CO); 1650 ($\text{C}=\text{C}$); 950 and 820 ($=\text{CH}_2$).

^1H -NMR (Cl_3CD , 300 MHz), ppm: 1.32 (3H, t, $J = 7$ Hz, CH_2-CH_3); 3.11 (1H, t, $J = 6$ Hz, OH); 4.24 (2H, q, $J = 7$ Hz, CH_2-CH_3); 4.32 (2H, bd, $J = 6$ Hz, CH_2OH); 5.85 (1H, q, $J = 1.5$ Hz, $\text{HC}=\text{C}$); 6.26 (1H, dt, $J = 1.5$ and 0.9 Hz, $\text{HC}=\text{C}$).

^{13}C -NMR (Cl_3CD , 75 MHz) ppm: 13.81 (CH_3-CH_2); 60.54 (CH_2OH); 61.61 (CH_3-CH_2); 124.88 ($\text{CH}_2=\text{C}$); 139.46 ($\text{CH}_2=\text{C}$); 166.07 (CO).

Polymerization

All experiments were carried out in Pyrex glass dilatometers, previously calibrated and sealed off at high vacuum. EHMA was polymerized at 50°C in a thermostatic bath, regulated with a precision of $\pm 0.1^\circ\text{C}$, using AIBN ($[\text{I}] = 1.5 \times 10^{-2}$ mol/L), and THF as solvent ($[\text{M}] = 3.0$ mol/L). After the desired time, the reaction mixture was transferred to a vessel with a large excess of diethyl ether and the precipitated polymer was filtered off, washed with

diethyl ether and dried at reduced pressure until constant weight.

Copolymers of MMA with EHMA were prepared by free-radical polymerization of mixtures of both monomers with different composition, in THF at 50°C. As in the homopolymerization, the global concentration of monomers was 3.0 mol/L and the concentration of AIBN was 1.5×10^{-2} mol/L. The copolymer samples were isolated after the desired polymerization time, by pouring the reaction mixture in a large excess of ether. The precipitated samples were filtered off, washed with ether, and dried at reduced pressure until constant weight.

Characterization

Glass transition temperature of poly(ethyl α -hydroxymethylacrylate) was determined by DSC with a Perkin-Elmer DSC-4 equipment.

IR was recorded on a Perkin-Elmer 457 and ^1H -NMR spectra were recorded at 50°C in deuterated chloroform, 25% (w/v) (TMS as internal reference) with a Varian XL-300 spectrometer operating at 300 MHz. The relative areas of peaks were measured by means of the electronic integrator.

In order to get ^{13}C -NMR of the monomer, the same NMR spectrometer operating at 75 MHz was used.

RESULTS AND DISCUSSION

Homopolymerization of Ethyl α -Hydroxymethylacrylate

Ethyl α -hydroxymethylacrylate was polymerized at 50°C in solution of THF, $[\text{M}] = 3$ mol/L, using AIBN as a free-radical initiator, $[\text{I}] = 1.5 \times 10^{-2}$ mol/L. Methyl methacrylate was also polymerized under the same experimental conditions to provide comparative results.

The overall rates of homopolymerization, determined dilatometrically were 18.6×10^{-5} and 3.9×10^{-5} mol L⁻¹ s⁻¹ for EHMA and MMA, respectively. The value of the overall rate for MMA is in agreement with the theoretical value (3.57×10^{-5} mol L⁻¹ s⁻¹) calculated from the rate coefficients of propagation, termination for MMA polymerization, and decomposition rate of AIBN as reported by Tullig and Tirrell,¹⁹ assuming the efficiency factor of 0.6 reported by Brooks²⁰ for the AIBN-initiated homopolymerization of MMA.

The dilatometric data of EHMA have been analyzed by a nonlinear least-squares method previously described.²¹ The evaluated kinetic parameters,

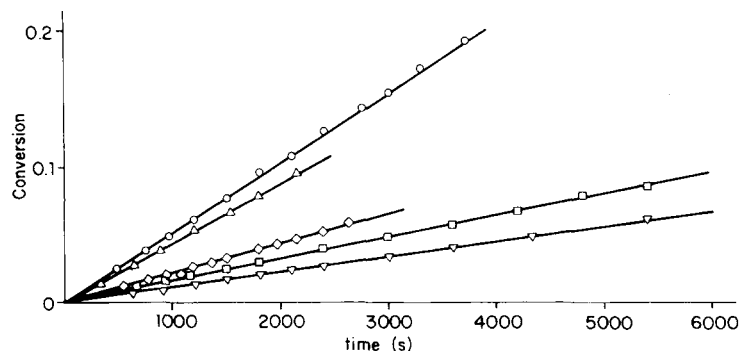


Figure 1. Radical copolymerization of MMA-EHMA systems in THF at 50°C. f_{MMA} : (∇) 1.0, (\square) 0.797, (\diamond) 0.486, (\triangle) 0.260, (\circ) 0.0.

assuming a value of f similar to that of MMA, i.e., $f = 0.6$, give the following values: $k_p/k_t^{1/2} = 0.62 \text{ L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$ and $k_d = 1.0 \times 10^{-6} \text{ s}^{-1}$ which are in agreement with those reported by Tulig and Tirrell¹⁹ for the thermal decomposition of AIBN at 50°C ($1.86 \times 10^{-6} \text{ s}^{-1}$). However, if we consider the f value reported by Ueda et al.¹³ for homopolymerization of EHMA in ethyl acetate initiated by AIBN, the $k_p/k_t^{1/2}$ parameter has a value of $0.53 \text{ L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$.

In any case the ratio $k_p/k_t^{1/2}$ for homopolymerization of EHMA is higher than those reported for the free-radical polymerization of MMA ($0.09 \text{ L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$),¹⁹ which could indicate a lower termination rate constant for EHMA than for MMA, since as pointed out by Mahabadi and O'Driscoll,²² the termination rate constant may be higher for the more flexible chains.

Although the flexibility of polymer chains has been traditionally expressed by the ratio of mean-square end-to-end distance of a polymer chain to that of the freely-joined chain, a qualitative indication of this parameter is given by the glass transition temperature (T_g). The T_g of poly(ethyl α -hydroxymethylacrylate) determined by DSC is 155°C, substantially higher than that of poly(methyl methacrylate). Moreover, the steric effect of the two α -substituents might cause a low reactivity of chain growing radical in the bimolecular termination reaction. In this way, Sato et al.²³ found a propagation rate constant of ethyl α -acetoacetoxymethylacrylate comparable to that of MMA, whereas the termination rate constant has a value smaller than that of MMA.

The differences observed between the $k_p/k_t^{1/2}$ value reported by Ueda et al.¹³ and the $k_p/k_t^{1/2}$ value found in this work could be due to a solvent effect²⁴ on both termination and propagation rate constant coefficients.

Copolymerization of Methyl Methacrylate with Ethyl α -Hydroxymethylacrylate

MMA was copolymerized with EHMA, using different monomer mixtures with MMA molar fraction ranging from 0.14 to 0.8. Conversions were measured dilatometrically, and then tested by gravimetry. Some of the obtained results are shown in Figure 1. As can be observed in Figure 1, conversions lower than 10% were obtained to satisfy the differential copolymerization equation. Rates of copolymerization were obtained from the slopes of straight lines and the overall concentration of monomers. As illustrated in Table I, the overall rate of copolymerization decreases as the MMA molar fraction in the feed increases.

The average molar composition of copolymers were determined by ¹H-NMR spectroscopy, considering the α -methyl resonance signals of the MMA and the methyl resonance signal of EHMA of the spectra shown in Figure 2, which also includes those of poly(methyl methacrylate) and of poly(ethyl α -hydroxymethylacrylate). The average molar com-

Table I. Composition and Kinetic Data of the Free-Radical Copolymerization of MMA-EHMA in THF Solution at 50°C

Sample	f_{MMA} (feed)	F_{MMA} (copolymer)	$R_p \times 10^{-6}$ (mol/L s)
1	1.000	1.000	3.9
2	0.797	0.806	4.8
3	0.664	0.666	5.4
4	0.578	0.598	6.6
5	0.486	0.503	7.1
6	0.392	0.370	12.9
7	0.260	0.230	15.9
8	0.140	0.110	18.6
9	0.000	0.000	18.6

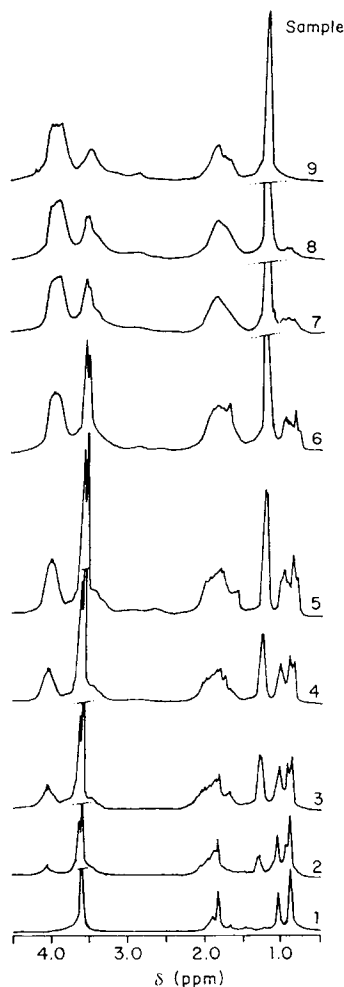


Figure 2. ^1H -NMR spectra of homopolymers and copolymers samples prepared by free-radical copolymerization of MMA-EHMA at 50°C . Number of sample corresponds to the composition indicated in Table I.

position of copolymers are quoted in Table I and the reactivity ratios have been determined through the nonlinear least-square analysis suggested by Tidwell and Mortimer.²⁵ The obtained values are $r_{\text{MMA}} = 1.264$ and $r_{\text{EHMA}} = 1.285$.

The 95% confidence limits are shown in Figure 3.

It is important to mention the rather unusual behavior of the MMA-EHMA system, since the reactivity ratio values obtained would indicate the possibility of block formation. Furthermore, the high value of $r_{\text{MMA}} \times r_{\text{EHMA}}$ indicates a low tendency of the monomers to alternate, so that the copolymer should be composed mainly of small sequences of the same type of monomeric units. Although these kind of results are not frequent, some systems appear in the literature, in which the calculated r_1 and r_2

values are both higher than one. In this connection, Saini et al.^{26,27} found values higher than one for reactivity ratios of methylmethacrylate-acrylamide, methylmethacrylate-methacrylamide, styrene-acrylamide, and styrene-methacrylamide systems, when the copolymerization is carried out in dioxane. Values for both r_1 and r_2 higher than one have also been reported by Johnston et al.²⁸ when free-radical copolymerization of styrene-acrylamide is carried out in acetonitrile. In contrast, reactivity ratios whose products $r_1 \times r_2$ are less than one are obtained for styrene-acrylamide or styrene-methacrylamide when ethanol or mixtures of dioxane-ethanol are used as solvents.²⁶⁻²⁸ Thus, it is clear that an effect of the solvent gives rise to changes in the reactivity ratios of styrene-acrylamide or styrene-methacrylamide systems. In this way, Harwood²⁹ has recently stated that the effect of solvents on reactivity ratios could be a consequence of the different partition coefficients of monomers in solution. The changes in reactivity ratios would be only apparent as a consequence of the local concentration of a determined monomer in the area of the chain growth radical may be different to that introduced in the feed. Therefore concerning the copolymerization of methyl methacrylate with ethyl α -hydroxymethylacrylate, the solvent (THF) might affect the local concentration of monomers in the proximity of the chain growth radical and, as a result, the found reactivity ratios can only be apparent.

However, as Berger and Kuntz³⁰ pointed out, sequence distribution analysis is necessary for discriminating among the alternative kinetic schemes

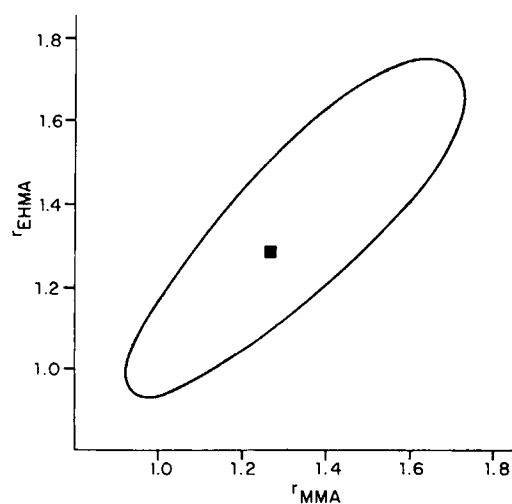


Figure 3. 95% confidence regions for MMA-EHMA reactivity ratios; estimate obtained using nonlinear regression.

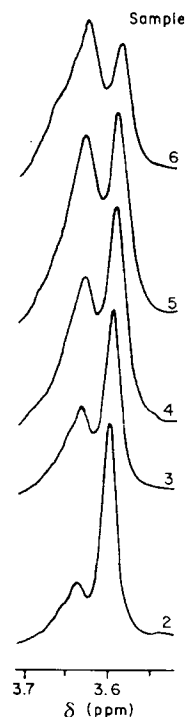


Figure 4. Expanded ^1H -NMR patterns of *O*-methyl resonance signals of MMA-EHMA copolymers. Number of sample corresponds to the composition indicated in Table I.

in copolymerization. As shown by Figure 2, the NMR pattern of copolymer samples exhibits different signals, the intensities of which are a function of the molar composition of monomers in the feed. In this

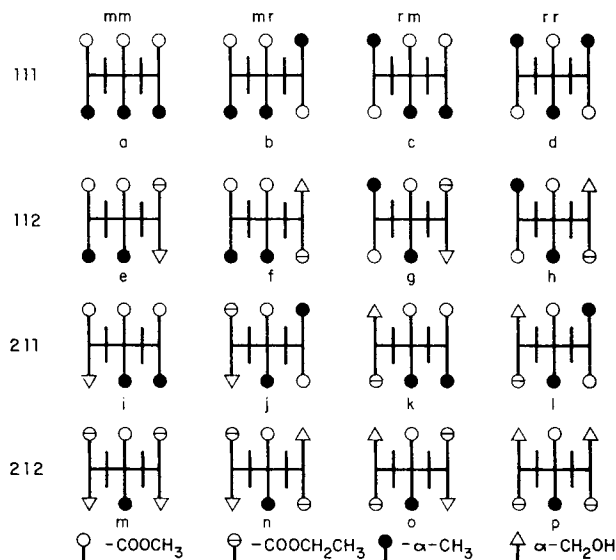


Figure 5. Schematic representation of MMA centered triads in MMA-EHMA copolymers.

Table II. Experimental and Calculated Relatives Intensities of the Resonance Lines of the *O*-Methyl Group of the MMA. Values Were Calculated with $r_{\text{MMA}} = 1.264$, $r_{\text{EHMA}} = 1.285$, $\sigma_{11} = 0.21$, and $\sigma = 0.20$

f_{MMA}	Relatives Intensities			
	3.60 ppm		3.64 ppm	
	Calcd	Experimental	Calcd	Experimental
0.797	0.75	0.71	0.25	0.29
0.664	0.60	0.56	0.40	0.44
0.578	0.50	0.49	0.50	0.51
0.486	0.41	0.41	0.59	0.59
0.392	0.32	0.33	0.68	0.67
0.260	0.20	—	0.80	—
0.140	0.12	—	0.88	—

way, as can be observed in Figure 4, the resonance signal of the *O*-methyl (MMA) is split into two peaks at 3.60 and 3.64 ppm. These signals could be analyzed on the basis of the stereochemical configuration of MMA centered triads shown in Figure 5, in which 1 and 2 indicate MMA and EHMA units, respectively. The peak at 3.60 ppm corresponds to the chemical shifts of *rr*, *mr* or *rm* and *mm* triads of poly(methyl methacrylate); consequently, we have assigned this peak to the same kind of 111 triads in the copolymer chain (a, b, c, and d triads in Fig. 5).

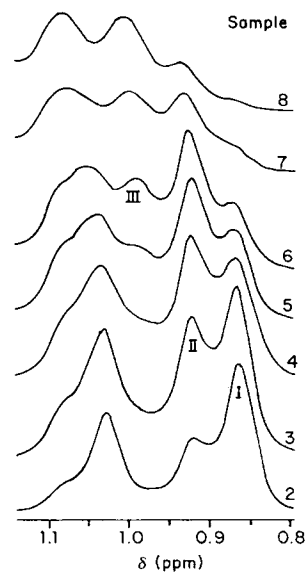


Figure 6. Expanded ^1H -NMR patterns of the α -methyl resonance signals of MMA-EHMA copolymers. Number of sample corresponds to the composition indicated in Table I.

Table III. Experimental and Calculated Relatives Intensities of the Resonance Lines of the α -Methyl Group of the MMA: Values Were Calculated with $r_{\text{MMA}} = 1.264$, $r_{\text{EHMA}} = 1.285$, $\sigma_{11} = 0.21$, and $\sigma = 0.20$

f_{MMA}	Relatives Intensities					
	III (0.98 ppm)		II (0.92 ppm)		I (0.87 ppm)	
	Calcd	Experimental	Calcd	Experimental	Calcd	Experimental
0.797	0.02	—	0.18	0.20	0.43	0.41
0.664	0.05	—	0.26	0.27	0.32	0.32
0.578	0.09	—	0.29	0.30	0.25	0.22
0.486	0.13	0.12	0.31	0.32	0.18	0.17
0.392	0.19	0.20	0.31	0.31	0.13	0.12
0.260	0.31	0.27	0.27	0.26	0.06	0.08
0.140	0.44	0.41	0.18	0.15	0.02	—

The same peak has also been attributed to triads e, g, i, j, and m, since the substitution of the carbomethoxy group for the carboethoxy group does not change the chemical shift of the *O*-methyl central group.

The peak at 3.64 ppm has been assigned to f, h, k, l, n, o, and p triads (Fig. 5), which have one or two CH_2OH groups surrounding the *O*-methyl central group and therefore its resonance can be shifted to downfield.

The assignment of the peaks to different triad sequences were confirmed by comparing both the experimentally determined triad fraction and those calculated theoretically using Bernoullian statistics with the isotactic parameters σ_{11} , $\sigma_{12} = \sigma_{21} = \sigma$ as defined by Bovey³¹ and Coleman,³² where σ_{ij} is the probability of generating a meso diad between an *i* ending growing radical and the incoming *j* monomer.

The value of $\sigma_{11} = 0.21$ was calculated from the α -methyl resonance signals of poly(methyl methacrylate) (Fig. 2). Considering Bernoullian statistics, the parameter σ can be calculated from the relative intensities of the peaks at 3.60 and 3.64 ppm in one of the considered spectra. The value $\sigma = 0.20$ was obtained from the spectrum corresponding to the copolymer prepared with 0.486 MMA molar fraction in the feed (sample 5, Fig. 4). These values, σ_{11} and σ , together with those of the conditional probabilities calculated from the quoted reactivity ratios, were used in order to calculate the theoretical intensities of the *O*-methyl resonance lines, for each copolymer sample. In Table II are quoted the obtained results except those for the MMA molar fraction in the feed lower than 0.3, in which the split of the resonance signals was not accurately resolved. The excellent agreement between calculated and

experimental data supports the assignment suggested.

On the other hand, as shown by Figure 6, the α -methyl resonance signals splits into several peaks, the intensity of which varies with the molar fraction of monomers in the feed. Peak I (0.87 ppm) corresponds to the chemical shift of *rr* triads of poly(methyl methacrylate); consequently, this peak has been assigned to triad d (Fig. 5) in the copolymer chain. Peak II (0.92 ppm) was assigned to the triads h and l, and peak III (0.98 ppm) to the triad p (Fig. 5), since the substitution of carbomethoxy group by carboethoxy group can shift the signal to downfield. The effect is additive and it can be observed that the substitution of one carbomethoxy group shifts the signals 0.05 ppm, whereas substitution of two carbomethoxy groups shifts the signals 0.11 ppm. The other peaks were not assigned because the resolution of the spectra is not good enough to be analyzed accurately. The assignment mentioned can be confirmed in the same way as those for the *O*-methyl signals, i.e., by calculating the theoretical relative intensities of the considered triads with the parameter values used previously. The theoretical and the experimental results are quoted in Table III. As can be seen, a good agreement between both series of values is obtained, which ratifies not only the assignment of the resonance signals but also the values of reactivity ratios obtained in THF solutions.

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