Radical Polymerization of Isomeric Methacrylic Monomers: *cis*- and *trans*-(2-Phenyl-1,3-dioxan-5-yl) Methacrylate

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ABSTRACT: Two new monomers, *cis*-(2-phenyl-1,3-dioxan-5-yl) methacrylate (CPDM) and *trans*-(2-phenyl-1,3-dioxan-5-yl) methacrylate (TPDM), have been synthesized. The stereochemical configuration in both monomers was unequivocally assigned by correlation $^{1}H-^{13}C$ NMR experiments. The radical polymerization reactions of both monomers were studied by ultraviolet spectroscopy and electron paramagnetic resonance spectroscopy to determine the polymerization rate parameter $k_p/k_t^{1/2}$ and the absolute propagation and termination rate constants (k_p and k_t) at different temperatures. The values of $k_p/k_t^{1/2}$ lie in the range 0.40−0.55 $L^{1/2}/(mol^{1/2}\ s^{1/2})$ for CPDM and 0.29−0.37 $L^{1/2}/(mol^{1/2}\ s^{1/2})$ for TPDM at temperatures between 45 and 70 °C, showing that the polymerization rate of the cis monomer with the substituents in equatorial−axial positions on the dioxane ring is higher than that of its trans counterpart with the phenyl and ester residue in equatorial positions on the dioxane ring. Using EPR measurements of the polymer radical concentrations, similar values for k_p were obtained for both trans and cis monomers, whereas the termination rate constant of the trans monomer was about twice that of the cis monomer at the same temperature.

Introduction

One of the most important topics of research in radical polymerization is the study of the relationship between structure and reactivity, from both theoretical and experimental points of view. Despite the ever-increasing research in this field, only a few works have studied theoretically the influence of chemical composition on the kinetic parameters involved in these reactions. Particularly, Gilbert et al., starting from the transition-state theory and using "ab initio" molecular orbital theory, studied the propagation rate constants of ethylene,[1,2] acrylonitrile, and methacrylonitrile.[3] These authors used their theoretical results to explain the systematic differences in the frequency factors and activation energies found in a homologous series of alkyl acrylates and methacrylates. On the other hand, the correlation between structure and reactivity requires reliable values of the propagation and termination rate constants. The values of rate constants can be determined by rotating sector,[4,5] EPR,[6,7] or pulsed laser[8−14] polymerization techniques, although the values do not agree well.

To gain deeper insight into the relationship between structure and reactivity in acrylic and methacrylic monomers, it is important to study the influence of bulky group on the reactivity. The polymerizations of different methacrylic esters with cyclo, bicyclo, tricyclo, fused ring, and even monomers with configurational isomerism in the side chain have already been studied by EPR spectroscopy,[7] and it was observed that the presence of bulky groups increases the radical concentration with respect to that of alkyl methacrylates, due to decrease in the termination rate constants, whereas the propagation rate constants are generally similar.

Previously, we studied[15] the radical polymerization at 60 °C of two new monomers bearing two bonded cycloaliphatic rings on the ester residue: *cis*-(2-cyclohexyl-1,3-dioxan-5-yl) methacrylate (CCDM) and *trans*-(2-cyclohexyl-1,3-dioxan-5-yl) methacrylate (TCDM). The termination rate constants were affected much more by the configuration of the monomer than the propagation rate constants. Continuing this research, this work studies the radical polymerization of *cis*- and *trans*-(2-phenyl-1,3-dioxan-5-yl) methacrylates (CPDM and TPDM) by ultraviolet (UV) and electron paramagnetic spectroscopy (EPR) and analyzes the influence of the cis/trans isomerism on the propagation (k_p) and termination rate constants (k_t) at different temperatures. It also compares the kinetic behavior of these monomers with that for CCDM and TCDM.

Experimental Section

Materials. Methacryloyl chloride (Fluka, 97%), benzaldehyde (Fluka, 99%), triethylamine (Fluka, 99,5%), and TEMPOL (Aldrich 98%) were used as received. Glycerol (Aldrich, 99%) and ethyl ether (SDS, 97%) were purified by conventional methods. 2,2′-Azobis(isobutyronitrile), AIBN (Fluka, 98%), was recrystallized from methanol and dried under high vacuum at room temperature.

Techniques. The NMR spectra of monomers and polymers were recorded on a Varian INOVA 400 spectrometer operating at 399.92 MHz (^{1}H) and 100.57 MHz (^{13}C), using deuterated chloroform or deuterated benzene as solvent and TMS as internal standard. Homonuclear 2D spectra (COSY) were acquired in the phase-sensitive mode. Data were collected in a 2048 × 512 matrix with a spectral width of 2756 Hz and 1.2 s of relaxation delay and then processed in a 2048 × 1024 matrix. 2D inverse proton detected heteronuclear one-bond

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shift correlation spectra were obtained using the HMQC pulse sequence. Data were collected in a 2048 × 512 matrix with a spectral width of 2756 Hz in the proton domain and 16 550 Hz in the carbon domain and were processed in a 2048 × 1024 matrix. The experiment was optimized for one bond heteronuclear coupling constant of 150 Hz. The HMBC experiment was acquired under the same conditions optimized for long-range coupling constants of 7 Hz.

The product mixtures and purity of monomers were analyzed by gas chromatography with mass spectrometric detection (GC/MS 5890 series II Hewlett-Packard apparatus equipped with a Hewlett-Packard HP1 capillary column) and by high-performance liquid chromatography (HPLC WATERS PUMP model 510 fitted with a Waters Nova-Pak C18 3.9 × 150 mm, column operating at 1 mL/min with a UV Waters 486 tunable absorbance detector).

The thermal properties of monomers and polymers were determined calorimetrically with a Perkin-Elmer DSC8 calorimeter at a heating rate of 10 °C min^{-1}.

A Varian Cary3-Bio UV−vis spectrophotometer with temperature controlled at ±0.05 °C was used to control the changes in absorbance during the polymerization reactions.

The number- and weight-average molecular weights of different samples of the polymers taken from the EPR experiments were determined by size exclusion chromatography (SEC). The measurements were performed at 25 °C in a Waters 150-C equipment with tetrahydrofuran solvent. Samples of polystyrene with uniform molecular weight in the range $1.8 \times 10^3 - 2.3 \times 10^6$ Da were used as a standard. The columns were PL gel 5 μm mixed bed, and the flow rate was 1 mL min^{-1}. A differential refractive index detector and a differential viscometer Viscotech 110 were coupled at the end of the column.

The concentrations of the radical species in the polymerization reactions were determined by electron spin resonance (EPR). The EPR spectra were recorded on benzene solutions at variable monomer and initiator concentrations in 3 mm diameter quartz tubes at temperatures in the range 50−70 °C by using a Bruker ESP 300 spectrometer. The conditions to register the spectra were the following: microwave frequency, 9.5 GHz; modulation frequency, 100 kHz; modulation amplitude, 3 G; conversion time, 40 ms; time constant, 655 ms; sweep time, 42 s; power, 6.32 mW; receiver gain 3×10^5; scan number, 5.

Monomer Syntheses. The monomers were prepared by reaction between methacryloyl chloride, glycerol, and benzaldehyde, according to the procedure shown in Scheme 1.

1. Syntheses of the Acetals. In the first step, glycerol (88.5 g) reacted with benzaldehyde (100 g) using hydrogen chloride as catalyst (0.1 mL), at 25 °C, and with water removal up to the end of the reaction (90 min). The yield of acetals in the reaction was about 90%. The acetals mixture was distillated (85−90 °C; 0.1 mmHg), and the product was characterized by gas chromatography (GC). The reaction gives rise to two different alcohol−acetals: the first one containing the 1,3-dioxolane ring and the other the 1,3-dioxane ring, both acetals being mixtures of the corresponding cis and trans isomers.

2. Esterification of the Acetals. The following step involved the reaction between the mixture of acetals (60 g) and methacryloyl chloride (32.6 mL). This reaction was carried out in dried ethyl ether under a nitrogen atmosphere at 0 °C, for a period of 30 min, and neutralizing the hydrogen chloride evolved with triethylamine (40.5 g). The yield of this reaction was 60%. Flash chromatography was used for the purification process of the mixture of monomers, thus separating the two configurational isomers *cis*-(2-phenyl-1,3-dioxan-5-yl) methacrylate (CPDM) and *trans*-(2-phenyl-1,3-dioxan-5-yl) methacrylate (TPDM) which were further crystallized from absolute ethanol. The final yield in CPDM and TPDM was about 30%, referred to the mixture of acetals.

The monomers thus obtained have purity higher than 99% as determined by HPLC and GC.

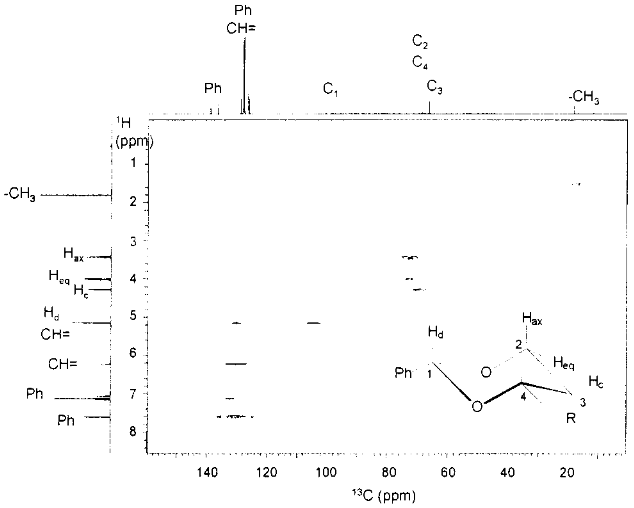
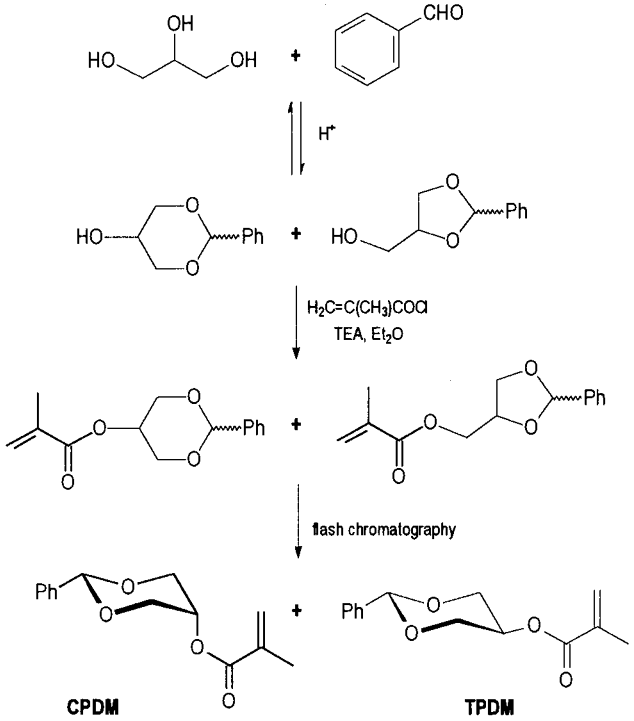


Figure 1. Heteronuclear shift correlation spectrum (benzene-d_6) of *cis*-(2-phenyl-1,3-dioxan-5-yl) methacrylate (CPDM).

Scheme 1



The melting points, T_m, enthalpies, ΔH_m, and entropies of fusion, ΔS_m, of monomers were 62 and 89 °C, 5100 and 6900 cal mol^{-1}, and 14.9 and 19.1 cal mol^{-1} K^{-1} for CPDM and TPDM, respectively.

The ^{1}H and ^{13}C NMR spectra (Figures 1 and 2) show the following chemical shifts corresponding to the resonances of different protons and carbons for CPDM and TPDM: CPDM (bz, TMS), ^{1}H NMR: δ = 1.79 ppm (s, 3 H), 3.41 ppm (m, 2 H), 4.00 ppm (m, 2 H), 4.27 ppm (m, 1 H), 5.14 ppm (s, 1 H), 5.15 ppm (s, 1 H), 6.23 (s, 1 H), 7.00−7.60 ppm (m, 5 H), ^{13}C NMR: δ = 18.2 ppm (−CH_3), 65.8 ppm (−O−CH−O−), 68.8 (−CH_2−O−), 100.8 ppm (-**C**H−O−CO−), 126−138 ppm (−C_{ar} and CH=), 167.3 ppm (−C=O). TPDM ($CDCl_3$, TMS), ^{1}H NMR: δ = 1.94 ppm (s, 3 H), 3.74 ppm (m, 2 H), 4.43 ppm (m, 2 H), 5.07 ppm (m, 1 H), 5.46 ppm (s, 1 H), 5.60 ppm (s, 1 H), 6.11 (s, 1 H), 7.35−7.50 ppm (m, 5 H), ^{13}C NMR: δ = 19.2 ppm (−CH_3), 64.1 ppm (−O−CH−O−), 69.6 (−CH_2−O−), 102.4 ppm (-**C**H−O−CO−), 126−138 ppm (−C_{ar} and CH=), 167.3 ppm (−C=O).

Polymerizations. Radical polymerizations of *cis*-(2-phenyl-1,3-dioxan-5-yl) methacrylate (CPDM) and *trans*-(2-phenyl-1,3-

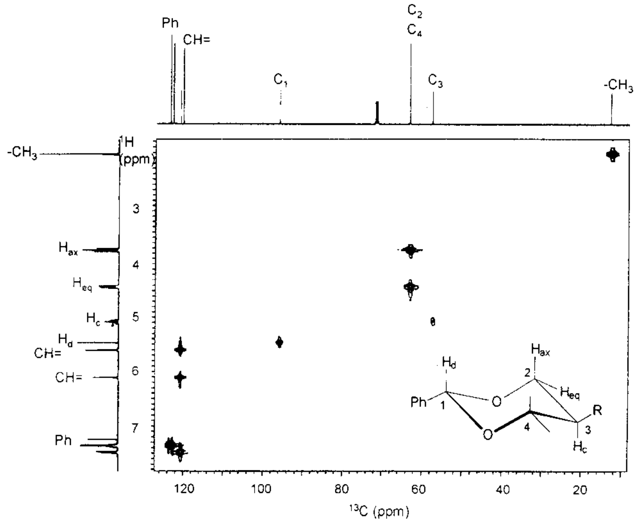


Figure 2. Heteronuclear shift correlation spectrum ($CDCl_3$) of *trans*-(2-phenyl-1,3-dioxan-5-yl) methacrylate (TPDM).

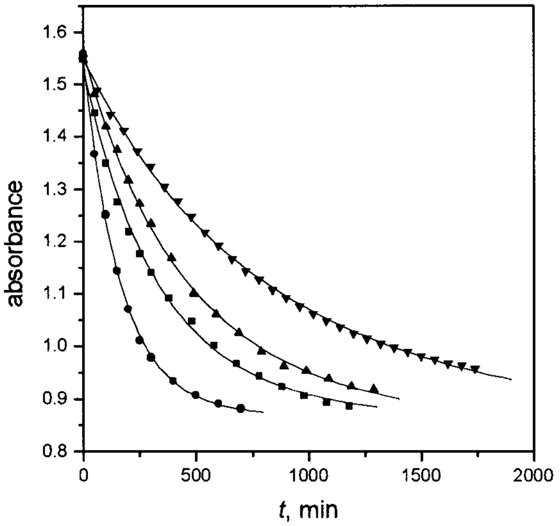


Figure 3. Changes in the absorbance time at 274 nm for the radical polymerization of *trans*-(2-phenyl-1,3-dioxan-5-yl) methacrylate at 65 (●), 55 (■), 50 (▲), and 45 °C (▼) ($[M_0] = 0.6$ mol L^{-1}, $[I_0] = 0.01$ mol L^{-1}).

dioxan-5-yl) methacrylate (TPDM) were carried out in dioxane at temperatures between 45 and 70 °C, using AIBN as initiator. The concentration of monomer and initiator was in all the experiments 0.6 and 0.01 mol L^{-1}, respectively. Some additional experiments were carried out in benzene solution by using variable concentrations of monomer and initiator lying in the ranges 1−2 and 0.05−0.15 mol L^{-1}, respectively. The EPR spectra were only registered under these last conditions.

The polymerization were followed by measuring changes in the monomer concentrations by UV spectroscopy. Absorbances in the region between 270 and 280 nm are characteristic of the monomers and are not affected by the initiator decomposition during the polymerization reactions. These absorptions follow the Lambert−Beer law in the range of monomer and polymer concentrations used. Monomer conversion measured by UV spectroscopy was checked by gravimetric methods, and the two techniques agreed well.

Figure 3 shows changes in absorbance with time in the TPDM polymerization at different temperatures, and Figure 4 shows conversion with time reaction in the polymerization of the two monomers in the same conditions.

An example of these reactions is the following: 0.041 g (0.01 M) of AIBN and 3.72 g (0.6 M) of TPDM were dissolved in dioxane in a 25 mL flask. A 3 mL aliquot of this solution was introduced in a UV quartz cell; oxygen was previously eliminated by bubbling nitrogen into the solution. The reaction was carried out at 55 °C up to 93% of conversion (980 min).

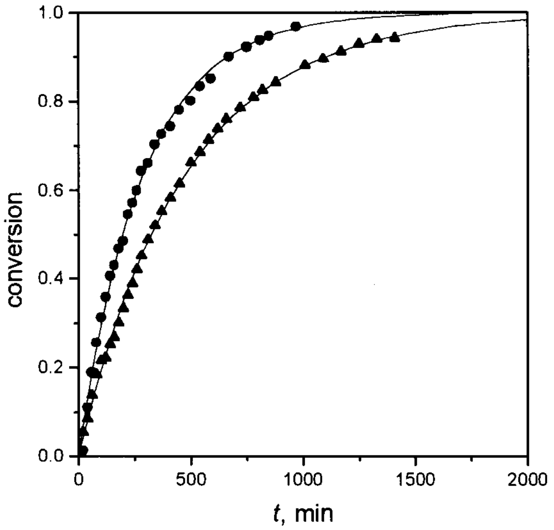


Figure 4. Comparison of the conversion dependence on time in the polymerization of both monomers CPDM (●) and TPDM (▲) at 50 °C ($[M_0] = 0.6$ mol L^{-1}, $[I_0] = 0.01$ mol L^{-1}).

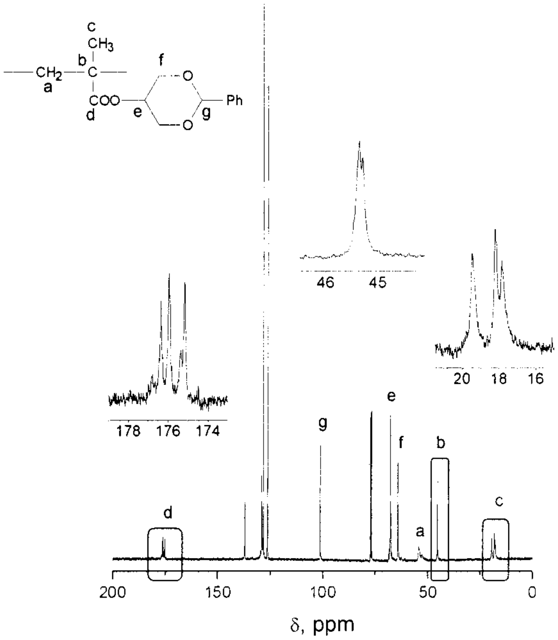


Figure 5. ^{13}C NMR spectrum ($CDCl_3$) of poly[*trans*-(2-phenyl-1,3-dioxan-5-yl) methacrylate].

The polymer was isolated from the reaction medium by several precipitations in *n*-hexane and finally was purified by freeze-drying from dioxane solution. The number-average molecular weight, M_n, of this sample of PTPDM was 3.28×10^5 Da with an I_p index, M_w/M_n, of 2.02, M_w being the weight-average molecular weight. The ^{13}C NMR spectrum of this polymer is shown in Figure 5. (The NMR spectra of the polymers are independent of the molecular weight of the sample.)

Results and Discussion

Characterization of the Monomers. The characterization of CPDM and TPDM was performed by ^1H and ^{13}C NMR spectroscopies, and the assignment of the ^1H and ^{13}C spectra for CPDM and TPDM was carried out by homonuclear and heteronuclear two-dimensional

Table 1. Kinetic Constants, Determined by UV Spectroscopy, for the Polymerizations of *cis*- and *trans*-(2-Phenyl-1,3-dioxan-5-yl) Methacrylate[a]

	$k_p/k_t^{1/2}$, $L^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$		
T, °C	CPDM	TPDM	$k_d \times 10^6$, s^{-1}
70	0.54_7	0.37_0	36.5
65	0.51_8	0.35_5	18.6
60	0.49_4	0.34_4	9.15
55	0.46_3	0.32_7	4.54
50	0.43_6	0.31_2	2.18
45	0.40_2	0.29_2	1.06

[a] The fourth column lists the values of k_d used for the simulation.[16-19]

experiments. Figures 1 and 2 show the HMQC spectra for CPDM and TPDM, respectively, and their assignments.

The stereochemistry at C_1 and C_3 was unequivocally determined by NOESY experiments which correlate the spatial position of the nearby protons. Thus, for CPDM monomer, irradiation of the H_c proton (4.27 ppm) enhanced the H_{ax} and H_{eq} protons at 3.41 and 4.00 ppm, respectively. Similarly, irradiation of the H_d proton (5.14 ppm) enhanced the axial protons on C_2 and C_4 (3.41 ppm.). For TPDM monomer, irradiation of the H_c proton (5.07 ppm) enhanced the H_{eq} protons (4.43 ppm), and irradiation of the H_d proton (5.46 ppm) enhanced the ester protons and the axial protons on C_2 and C_4 (3.74 ppm).

Kinetics of Polymerization. The data of the polymerization kinetics followed by UV spectroscopy were analyzed using eq 1, which is straightforward derived from the classical radical polymerization scheme by assuming equal initiation and termination rates,

$$\ln \frac{[\mathrm{M}_0]}{[\mathrm{M}]} = 2k_p\left(\frac{2f[\mathrm{I}_0]}{k_t k_d}\right)^{1/2}\left[1-\exp\left(-\frac{k_d t}{2}\right)\right] \qquad (1)$$

k_d, k_p, and k_t are the rate constants for initiator decomposition, propagation, and termination reactions, respectively, $[M_0]$ and $[M]$ are the initial and instantaneous concentrations of monomer, $[I_0]$ is the initial concentration of initiator, and f is the efficiency of the initiator.

The ratio between the initial and instantaneous monomer concentrations is equivalent to $(A_0 - A_\infty)/(A - A_\infty)$, where A_0, A, and A_∞ are respectively the absorbances of the monomer at the wavelength considered at the start of the reaction, at time t, and at total conversion. Therefore, eq 1 can be transformed into eq 2.[15]

$$A = A_\infty + (A_0 - A_\infty) \times \exp\left\{-2k_p\left(\frac{2fI_0}{k_t k_d}\right)^{1/2}\left[1-\exp\left(-\frac{k_d t}{2}\right)\right]\right\} \qquad (2)$$

Computer simulations of the absorbance data according to eq 2 can be used to determine A_∞ and $k_p/k_t^{1/2}$. The values of k_d (Table 1) for the calculations at each temperature were taken from the literature,[16-19] and those of f were determined as indicated below. Very good simulations were obtained in all of the reactions as seen in the example of Figure 3. This indicates that no anomalous deviations[20] of the normal kinetics were observed up to high conversions, at least at the concentration of monomer used in the experiments.

Table 2. Molecular Weights Average and Polydispersity Indexes for PCPDM and PTPDM[a]

	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$	I_p
PCPDM	1.38	2.38	1.72
PTPDM	0.92	2.12	2.3

[a] These samples were synthesized at 60 °C and under equal monomer and initiator concentration of 1 and 0.1 mol L^{-1}.

Once A_∞ was known, the fractional conversions were calculated from the values of A_0, A, and A_∞ , and the results for both monomers are compared in Figure 4. The curves show the time dependence of the conversion for the polymerization of the monomers; CPDM is more reactive than TPDM. These findings are quantitatively expressed with the values of $k_p/k_t^{1/2}$, which are listed in Table 1 for different temperatures. Almost double values of $k_p/k_t^{1/2}$ were obtained for CPDM, indicating a very important effect of the substitution (axial or equatorial) in the 1,3-dioxane ring on the polymerization rates.

These results clearly show that the CPDM isomer is more reactive than the trans counterpart TPDM, as occurs in the polymerization of CCDM and TCDM methacrylate.[15] However, these results contradict those reported for the polymerization of *trans*- and *cis/trans*-4-*tert*-butylcyclohexyl methacrylate with cis content of 71%, which have similar polymerization rates.[21]

Characterization of the Polymers. The values of the glass transition temperatures (T_g) were 126 and 144 °C for poly[*cis*-(2-phenyl-1,3-dioxan-5-yl) methacrylate] (PCPDM) and poly[*trans*-(2-phenyl-1,3-dioxan-5-yl) methacrylate] (PTPDM), respectively.

The number- and weight-average molecular weights, M_n and M_w, and the polydispersity index I_p of the samples of PCPDM and PTPDM at conversion 20% are shown in Table 2.

The stereochemical configuration of methacrylic polymers was studied by NMR spectroscopy. As an example, the decoupled ^{13}C NMR spectra of PTPDM and PCPDM with the expanded parts corresponding to the carbons showing stereochemical sensitivity are shown in Figures 5 and 6. The assignment of the different signals that appeared in the spectra was made following conventional treatments,[22] and the carbon and proton chemical shifts for the triads and pentads are listed in Table 3 for both polymers. By deconvolution and integration of the different peaks, the molar fractions of tactic sequences were determined and are also shown in Table 3. Both polymers were predominantly syndiotactic with average values of syndiotactic dyads of 0.77. The values of the different dyads and triads indicate that the stereochemical sequences agree well with a Bernoulli distribution,[23] since $mm = m^2$, $mr = 2m \times r$, and $rr = r^2$.

EPR Kinetic Study and Temperature Dependence of k_p and k_t. Since the higher reactivity of CPDM compared to that of TPDM may be due to either higher k_p or lower k_t, we must determine the absolute rate constants in order to establish the true influence of the chemical structure on the propagation and termination reactions. Values of k_p and k_t can be obtained knowing the polymerization rate (already determined by UV spectroscopy) and the stationary concentration of free radicals by EPR spectroscopy,[6,7] which under certain conditions is an appropriate method to obtain reliable values of the kinetic constants.

Figure 7 shows the EPR spectra of the propagating radicals corresponding to the polymerization of CPDM,

Table 3. Molar Fractions and Chemical Shifts of the Different Dyads, Triads and Pentads for PCPDM and PTPDM

		PCPDM δ, ppm					PTPDM δ, ppm				
		molar fraction	^{1}H −CH$_3$	^{13}C −CH$_3$	^{13}C−-C−	^{13}C−CO−	molar fraction	^{1}H −CH$_3$	^{13}C −CH$_3$	^{13}C−C−	^{13}C−CO−
dyads	m	0.23					0.23				
r	0.77	0.77									
triads	mm	0.060	1.46	19.8	45.9		0.063	1.26	21.1	45.4	
mr	0.34_0	1.25	18.9	45.7	0.33_2	1.07	19.4	45.3			
rr	0.60_0	1.17	17.9	45.5	0.60_4	0.94	17.9	45.2			
pentads	mrrm	0.059				177.7	0.050				176.8
mrrr	0.13_4	177.4	0.20_4	176.4							
rrrr	0.36_9	177.2	0.34_7	175.9							

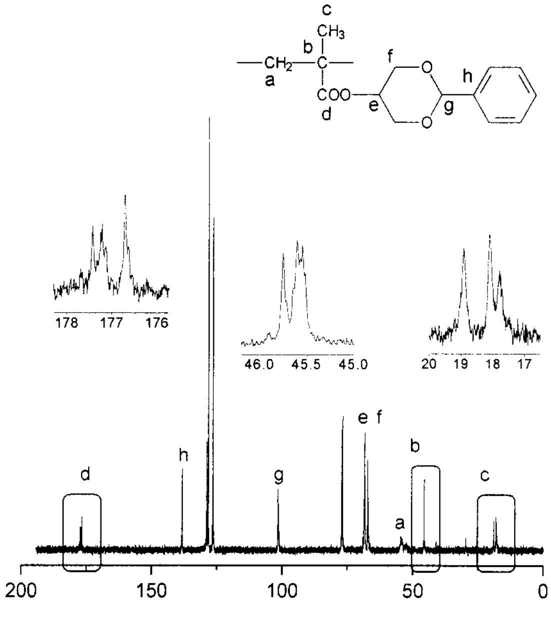


Figure 6. ^{13}C NMR spectrum (CDCl$_3$) of poly[*cis*-(2-phenyl-1,3-dioxan-5-yl) methacrylate].

TPDM, CCDM, and TCDM at 70 °C in benzene. The spectra, registered on solutions of equal initiator and monomer concentrations, show higher intensities of the resonance signals in the case of the cis monomers, indicating lower values of the termination rate constant.

The EPR spectra of the cis (CPDM and CCDM) polymer radicals are more resolved than those of the trans isomers. This may be attributed to the more hindered structure of the trans radicals or to the tightening of the microsurroundings around propagating radicals as a consequence of different viscosities of the reaction media.[24] The latter possibility is very improbable due to the higher polymerization rates of the cis monomers (and correspondingly higher molecular weights) with respect to the trans monomers. However, the reported very good EPR spectral resolution of poly(3-[tris(trimethylsilyloxy)silyl]propyl methacrylate) radicals[25] is probably due to the exceptionally flexible chains of this polymer in comparison to other polymethacrylates, which is consistent with the first possibility.

The influence of temperature on the radical concentration is shown in the normalized spectra of Figure 8 for CPDM. The intensity of the spectral signals increases with temperature. This is probably due to an increase in the concentration of free radicals, where the effect of the increase in the initiation rate coefficient with temperature is greater than the opposite effect of the increase in the termination rate coefficient. Similar results were obtained for the polymerization of TPDM.

Typical 13-line spectra were obtained under different reaction conditions and at different reaction times and even at very high conversion. The 9-line spectrum was never observed, indicating that the change in the viscosity of the medium with polymerization does not seem to affect the mobility of the radicals as in MMA

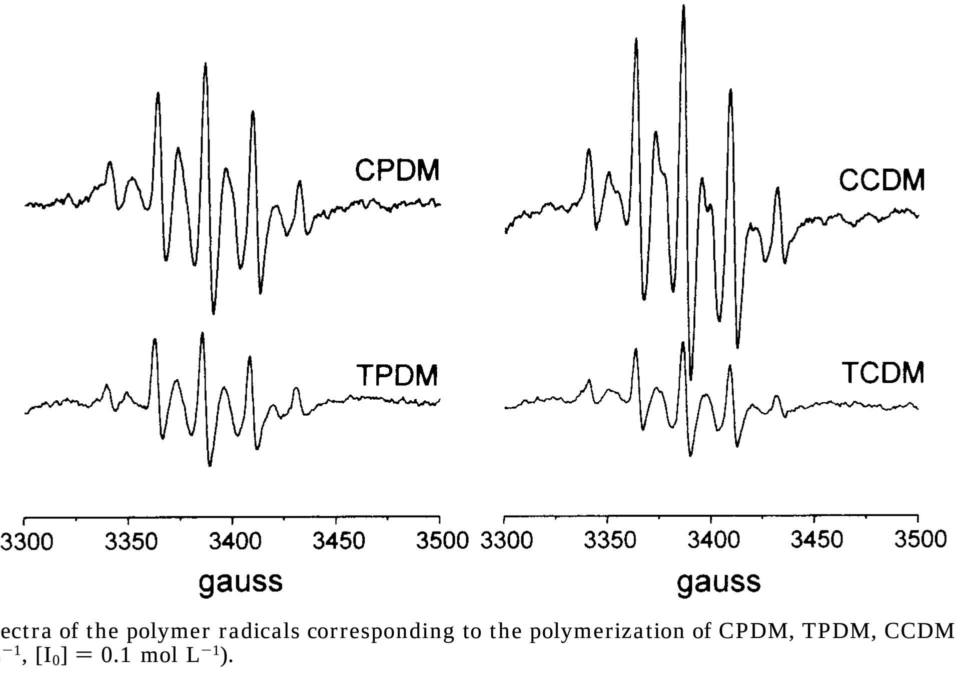


Figure 7. EPR spectra of the polymer radicals corresponding to the polymerization of CPDM, TPDM, CCDM, and TCDM at 60 °C ([M$_0$] = 1 mol L^{-1}, [I$_0$] = 0.1 mol L^{-1}).

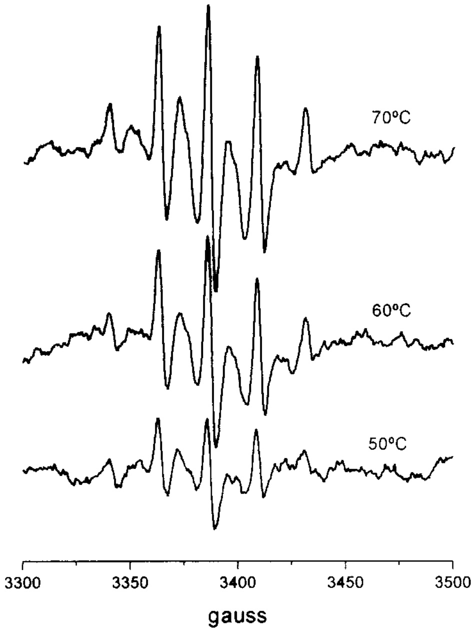


Figure 8. EPR spectra of the polymer radicals in the polymerization of CPDM at different temperatures ($[M_0] = 1$ mol L^{-1}, $[I_0] = 0.1$ mol L^{-1}).

where the EPR spectra of the polymerization system change from 13 to 9 lines.[7,26] This proves that the gel effect[27,28] is absent in the polymerization of both monomers.

The nature of the propagating species in the polymerization of other methacrylic monomers, especially methyl methacrylate, has been intensively studied.[29] For instance, Symons[30] and more recently Tonge et al.[31] showed that the EPR spectra of poly(methyl methacrylate) radicals observed under different polymerization conditions can be rationalized by considering two rotamers of a single free radical. The 9-line spectra, at high conversions, are adequately simulated with two different hyperfine coupling constants for the methylene protons corresponding to each rotamer and one coupling constant for the methyl protons. However, the normal 13 lines at low conversions require for the simulation two hyperfine couplings for the methylene protons and one for the corresponding methyl protons of the radical. It would be also possible to simulate the spectra corresponding to our radicals. The results of our simulation taking these considerations into account are shown in Figure 9 for the polymers radicals of CCDM. (The results for the rest of the monomers were very similar to that shown in this figure.) The best hyperfine couplings for the simulation of the 13-line spectrum were 22.53 G for the methyl protons and 13.96 and 8.94 G the two methylene protons. The latter values are similar to those reported by Tonge et al.[31] for the poly(methyl methacrylate) radicals at low conversions. The splitting patterns of the polymethacrylate radicals have been discussed by different researchers taking into account the restricted rotation around the C−C bond.[7,21,29−32] However, the treatment of Tonge et al.[31] applied to our polymer radicals is adequate to simulate the spectra. A deeper analysis of the splitting nature of the propagating radicals in our polymerizations is out of the scope of this work.

To quantify the radical concentration, the spectrum must be doubly integrated and compared with that corresponding to a stable radical. The double integration was carried out with correction of the baseline on both the normal first-derivative spectrum and the absorption spectrum. This, in our opinion, more correctly estimates the radical concentrations; in fact, the simulated 13-line spectra gave double-integration values very similar to those obtained with this method. This method also resembles that recently reported by Tonge et al.[32]

Double integration of the signals and comparison with the EPR spectrum of 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPOL) as a standard gives the radical concentrations at different reaction times (Figure 10). The radical concentration does not change with time in either polymerization, suggesting that under these experimental conditions the effect of viscosity on the rate constants is negligible.

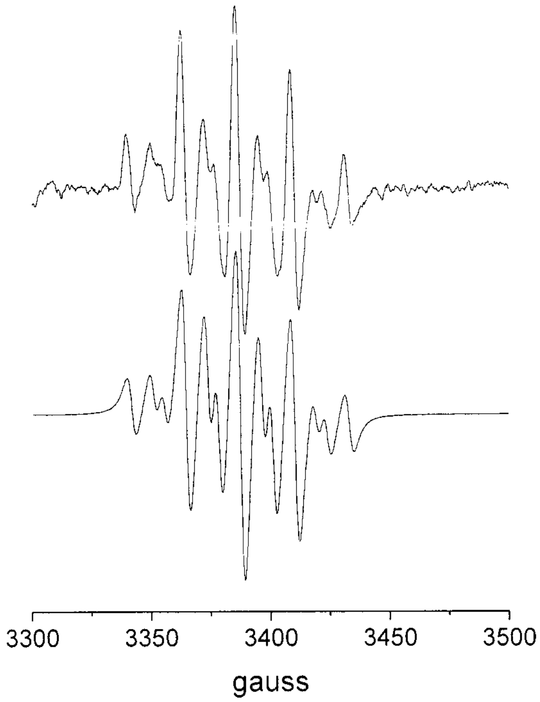


Figure 9. EPR spectra experimental (top) and simulated (botton) of the polymer radicals in the polymerization of CCDM at 60 °C ($[M_0] = 1$ mol L^{-1}, $[I_0] = 0.1$ mol L^{-1}).

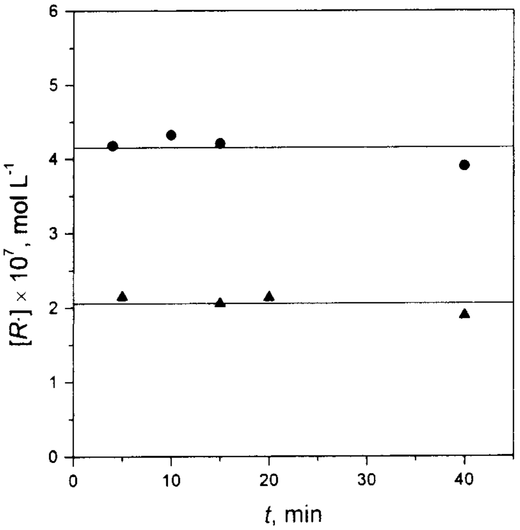


Figure 10. Time dependence of the radical concentrations in the polymerization of CPDM (●) and TPDM (▲) at 60 °C ($[M_0] = 1$ mol L^{-1}, $[I_0] = 0.075$ mol L^{-1}).

Table 4. Propagation and Termination Rate Constants for the Polymerizations of *cis*- and *trans*-(2-Phenyl-1,3-dioxan-5-yl) Methacrylate and *cis*- and *trans*-(2-Cyclohexyl-1,3-dioxan-5-yl) Methacrylate[a]

	k_p, L mol^{-1} s^{-1}				$k_t \times 10^{-6}$, L mol^{-1} s^{-1}			
T, °C	CPDM	TPDM	CCDM	TCDM	CPDM	TPDM	CCDM	TCDM
70	1639	1640	1510	1761	8.98	19.65	6.23	23.79
65	1316	1365	1273	1478	6.45	14.78	4.87	17.63
60	1067	1100	959	1163	4.66	10.22	2.97	11.23
55	851	837	799	1034	3.38	6.55	2.32	9.53
50	719	633	651	857	2.72	4.12	1.71	6.91

[a] Values are averages from at least five experiments, with errors of approximately 15%.

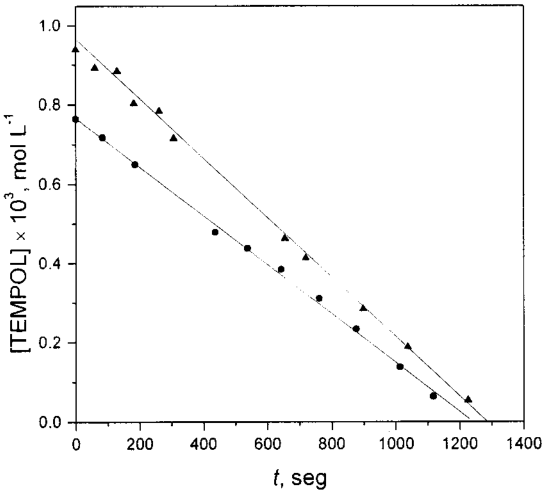


Figure 11. Concentration decay of TEMPOL in the 1 mol L^{-1} polymerization system at 60 °C of CCDM (●) ([I$_0$] = 0.075 mol L^{-1}) and CPDM (▲) ([I$_0$] = 0.1 mol L^{-1}) .

The radical disappearance rate is given by eq 3, where the termination rate is considered to be equivalent to $k_t[R^\bullet]^2$.

$$-\frac{d[R^\bullet]}{dt} = k_t[R^\bullet]^2 - 2f\,k_d[I] \tag{3}$$

In the stationary state, this equation equals zero. Therefore, to calculate the absolute values of the termination rate constants, the true value of the efficiency factor, *f*, must be determined. The values of *f* can be determined by trapping the radicals with a stable radical such as TEMPOL and measuring its time concentration decay, as shown in Figure 11 for the polymerization of CCDM and CPDM. The slopes of the straight lines are equivalent to $2f\,k_dI$, which corresponds to *f* values of 0.42 ± 0.02 for the polymerization of all of the monomers studied. This value is practically independent of temperature.

Since the steady-state radical concentration is practically constant with time, the values of k_t are easily obtained from eq 3. These values, together with those of $k_p/k_t^{1/2}$ determined by UV spectroscopy, allow the direct calculation of k_p. Within experimental error, there are no differences in the values of the propagation and termination rate constants for initiator concentrations varying from 0.05 to 0.15 mol L^{-1}.

The values of k_p and k_t determined at different temperatures in the polymerizations of CPDM and TPDM are compiled in Table 4, which also includes new values of k_p and k_t determined in the polymerizations of CCDM and TCDM. The values for CCDM and TCDM are higher than those previously reported[15] because our new method for correcting the baseline leads to lower values of the radical concentrations than those obtained by a simple baseline correction. Nevertheless, the conclusions[15] remain unchanged. The results in Table 4 demonstrate that the propagation rates are almost independent of the configuration of either monomer pairs, in contrast to the termination rate constants. The differences in the propagation rate constants are also minor if we compare monomers with the same configuration containing phenyl or cyclohexyl substituents on the dioxane ring. The configuration of the substituents on the dioxane ring in CPDM and TPDM and in CCDM and TCDM significantly affects the values of the termination rate.

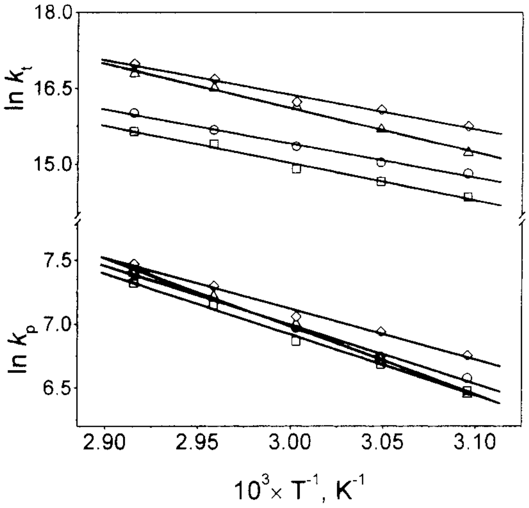


Figure 12. Arrhenius plots of the propagation and termination constants for the polymerization of CPDM (○), TPDM (△), CCDM (□), and TCDM (◇).

Table 5. Arrhenius Parameters for the Polymerizations of *cis*- and *trans*-(2-Phenyl-1,3-dioxan-5-yl) Methacrylate and *cis*- and *trans*-(2-Cyclohexyl-1,3-dioxan-5-yl) Methacrylate

	ln A_p, L mol^{-1} s^{-1}	E_p, kJ mol^{-1}	ln A_t, L mol^{-1} s^{-1}	E_t, kJ mol^{-1}
CPDM	20.84	38.6	35.56	56.2
TPDM	22.92	44.4	42.33	73.1
CCDM	21.19	39.8	37.12	61.6
TCDM	19.06	33.3	36.87	57.1

The measurements were made in a relatively narrow temperature range and therefore only approximate values of the activation energies and frequency factors can be obtained. Arrhenius plots of the experimental propagation and termination rate constants for the different monomers are shown in Figure 12, and the values of the activation parameters are listed in Table 5. The E_p values of alkyl methacrylate polymerizations[33] are about a half those in the polymerization of our monomers. Although the activation energies and/or frequency factors can adequately describe the reactivity of monomers in radical polymerizations, these kinetic

Table 6. Propagation and Termination Rate Constants Obtained by EPR Measurements for the Polymerization of Some Methacrylic Esters ($CH_2{=}C(CH_3)COOR$) Monomers at 60 °C

R	k_p, L mol^{-1} s^{-1}	$k_t \times 10^{-6}$, L mol^{-1} s^{-1}	reference
methyl	510	21	34
cyclohexyl	510	5.4	35
cyclohexyl	820	13.9	this work
trans-4-*tert*-butylcyclohexyl	550	1.9	21
cis/*trans*-4-*tert*-butylcyclohexyl	510	1.9	21
cis-2-*tert*-butylcyclohexyl	73	1.2	36
cis/*trans*-2-*tert*-butylcyclohexyl	64	0.9	36
trans-2-cyclohexyl-1,3-dioxanyl	1163	11.23	this work
cis-2-cyclohexyl-1,3-dioxanyl	959	2.97	this work
trans-2-phenyl-1,3-dioxanyl	1100	10.22	this work
cis-2-phenyl-1,3-dioxanyl	1067	4.66	this work

parameters, especially the frequency factor, are very sensitive to experimental errors in the usual narrow range of temperatures used in their experimental determination.

The values of k_p and k_t for several methacrylate monomers are listed in Table 6. Bulky groups decrease the termination rate constants significantly; the changes in propagation are unsystematic. Although we found that the values of k_t for the cis monomers are much lower than for the trans monomers, neither the propagation nor termination rate constants of other configurational monomers reported in the literature seem to be affected. In the case of the cyclohexyl methacrylate, we have determined k_p and k_t values higher than those reported by Matsumoto et al.[35] using the same technique, although the polymerization rate is practically equivalent.

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Supporting Information Available: ^{1}H NMR spectra of PCPDM and PTPDM, EPR spectra of polymer radicals corresponding to the polymerization of TPDM at different temperatures, and simulated EPR spectra of polymer radicals corresponding to the polymerization of CPDM, TPDM, and TCDM. This material is available free of charge via the Internet at http://pubs.acs.org.

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