0 to 300 °C at a rate of 10 °C/min. At high EMI-24 concentrations, the imidazole consumes most of the epoxide groups to form adducts. The T_g values for the 100.0 mol % and 50.0 mol % sample were determined to be 57 and 85 °C, respectively. As the EMI-24 concentration is lowered to 25.0 mol %, more epoxide groups are available for etherification and the T_g increases to 105 °C. The isothermal epoxide concentration profiles for 25.0 mol % EMI-24 show that complete conversion of the epoxide groups is obtained at 108 °C since the isothermal temperature exceeds the ultimate T_g of the system (see Figure 11). However, complete epoxide conversion does not occur for isothermal runs below 105 °C because the sample vitrifies when the T_g of the sample reaches the isothermal cure temperature. The highest T_g values of approximately 150 °C are obtained at EMI-24 concentrations of 7.0 and 5.0 mol %. As the EMI-24 concentration is reduced below 5.0 mol %, the T_g and the heat of reaction decrease rapidly and depend on the sample heating rate. As the heating rate decreases, the cure time increases, resulting in a higher heat of reaction and a higher T_g. The epoxy/imidazole adduct catalyzes the etherification reaction and contains the active sites for polymerization. At low imidazole concentrations, the etherification reaction rate is strongly dependent on the adduct concentration.

Conclusions

Dynamic and isothermal studies were used to identify and analyze the adduct and etherification reactions which occur during the cure of DGEBA with various 1-unsubstituted and 1-substituted imidazoles. The OH-adduct formation, which occurs only with the 1-unsubstituted imidazoles, was monitored by tracking the N–H stretching peak with IR analysis. The formation of a zwitterion adduct with an active alkoxide group occurred with all imidazoles. Overall, at imidazole concentrations of 25.0 mol % or less, the adduct formation was characterized by a slow rate of epoxide conversion compared to the rate of polymerization and by a constant T_g. The beginning of the O-etherification reaction, initiated by the alkoxide ion, was marked by a rapid increase in the T_g and by an increase in the rate of the epoxide conversion. Another etherification reaction, caused by the attack of an epoxide ring by a hydroxyl group, occurred in 1-unsubstituted imidazoles at low concentrations. The hydroxyl group was created during the OH-adduct formation through a rearrangement by a proton transfer from the 1-nitrogen. Therefore, OH-adduct reaction and the OH-etherification reaction were not observed for the curing reactions with the 1-substituted imidazoles.

The thermal properties of the network were shown to be strongly dependent on the imidazole concentration. At high imidazole concentrations (50 mol % and greater), the adduct reaction consumes most of the epoxide groups to form adducts. As the imidazole concentration is decreased, the T_g increases because fewer adducts are formed and more epoxide groups are available for chain growth and cross-linking. The maximum T_g is obtained for the DGEBA/EMI-24 system at about 5.0 mol % EMI-24. As the EMI-24 concentration is lowered below 5.0 mol %, the T_g decreases rapidly. At low imidazole concentrations, the rate of the etherification reaction decreased rapidly as the adduct concentration was decreased. The combination of DSC and FTIR studies and the use of model imidazoles has been shown to be an effective technique for analyzing the complex epoxy/imidazole curing process.

Acknowledgment. This research was supported by the I.B.M. Corporation. The epoxy resin was generously supplied by the Shell Development Co.

Registry No. DGEBA, 25068-38-6; EMI-24, 931-36-2; DMI-12, 1739-84-0; MI-1, 616-47-7; IMDZ, 288-32-4; (DGEBA)(EMI-24) (copolymer), 81855-87-0.

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Reactivity of Some Substituted Styrenes in the Presence of a Syndiotactic Specific Polymerization Catalyst

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ABSTRACT: The reactivities of several substituted styrenes have been tested, in the presence of a syndiotactic specific catalytic system consisting of tetrabenzyltitanium and methylalumoxane, by homopolymerization and copolymerization runs. I^+ substituents enhance the reactivity to a greater extent than was previously observed for isotactic polymerization. The stereospecificity is also affected by the substituents of the aromatic ring even when they are at the para position.

1. Introduction

Several substituted styrenes have been polymerized in the presence of homogeneous catalytic systems consisting of soluble titanium or zirconium compounds and methylalumoxane.[1-4] As previously reported, these catalytic systems promote polymerization of styrene to a syndiotactic polymer.[1-6]

In this paper we are reporting a comparison of the behavior in the polymerization of some substituted styrenes, i.e., styrene itself (S), *p*-methylstyrene (PMS), *m*-

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Table I[a]
Reactivities in Polymerization of Some Substituted Styrenes Relative to That of Styrene

monomer	amt, mmol	time, h	yield, mg	rel reactivities[b]
S	32.5	1.5	120	1.0
PMS	22	1.5	145	1.8
MMS	31	2.0	60	0.4
PMOS	36	0.5	1460	33.3
PCS	27	21.5	95	0.067
MCS	30	28	80	0.038
OCS	27	28	80	0.043

[a] All the polymerizations have been performed in the presence of tetrabenzyltitanium (2.5×10^{-5} mol) and methylalumoxane (0.200 g) in toluene (10 mL) at 50 °C under nitrogen atmosphere. [b] The reactivities are referred to that of styrene arbitrarely defined equal to 1.

Table II[a]
Polymerization Conditions and Compositions of the Binary Copolymers of Styrene with Para-Substituted Styrenes

comonomer	comonomer amt, mmol	yield, mg	time, h	f^b	F^c
PMS	14.8	60	0.5	1.17	0.53
PMS	14.8	230	0.5	1.76	0.85
PMS	7.4	100	0.5	2.31	1.1
PMS	7.6	60	0.5	2.75	1.3
PMS	9.1	210	0.5	3.23	1.7
PMS	6.4	170	0.5	4.34	2.1
PMS	7.6	210	0.5	4.69	2.4
PCS	39.2	360	20	0.42	3.0
PCS	34.5	210	24	0.24	1.1
PCS	47.2	150	24	0.17	0.65
PCS	61.6	140	24	0.14	0.43
PCS	61	120	24	0.11	0.29
PMOS	3.65	70	0.2	35.3	2.8
PMOS	3.65	90	0.2	23.8	1.8
PMOS	7.45	110	0.2	11.7	0.47
PMOS	14.6	400	0.2	5.9	0.20

[a] All the copolymerizations have been performed in the presence of tetrabenzyltitanium (2.5×10^{-5} mol) and methylalumoxane (0.200 g) in toluene (10 mL) at 50 °C under nitrogen atmosphere. [b] Composition of the feed (molar ratio of styrene to comonomer). [c] Composition of copolymer (molar ratio of styrene to comonomer).

methylstyrene (MMS), *p*-chlorostyrene (PCS), *m*-chlorostyrene (MCS), *o*-chlorostyrene (OCS), and *p*-methoxystyrene (PMOS), in the presence of the syndiotactic specific catalytic system tetrabenzyltitanium–methylalumoxane.

2. Experimental Section

All the monomers were purchased from Aldrich Chemie and distilled over calcium hydride under nitrogen atmosphere before using. Tetrabenzyltitanium and methylalumoxane were prepared according to the literature.[7,8] Both polymerizations and copolymerizations were performed under nitrogen atmosphere at 50 °C, by using toluene (10 mL), tetrabenzyltitanium (2.5×10^{-5} mol), and methylalumoxane (0.200 g). In Table I are reported the results of the homopolymerizations performed and the reactivities of the substituted monomer relative to styrene. The relative reactivities are evaluated for each monomer by comparing the homopolymerization yields under identical reaction conditions. The data concerning binary copolymerizations of styrene with *p*-methylstyrene and *p*-chlorostyrene are collected in Table II. All polymerizations were stopped by pouring the reaction mixture into acidified methanol. The homo- or copolymers were repeatedly washed with fresh methanol and dried in vacuo at 80 °C.

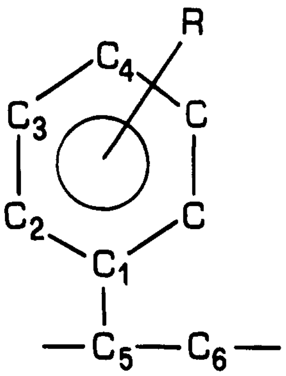

Figure 1. Numeration of the carbon atoms of the monomer units ($R = CH_3$, Cl, OCH_3).

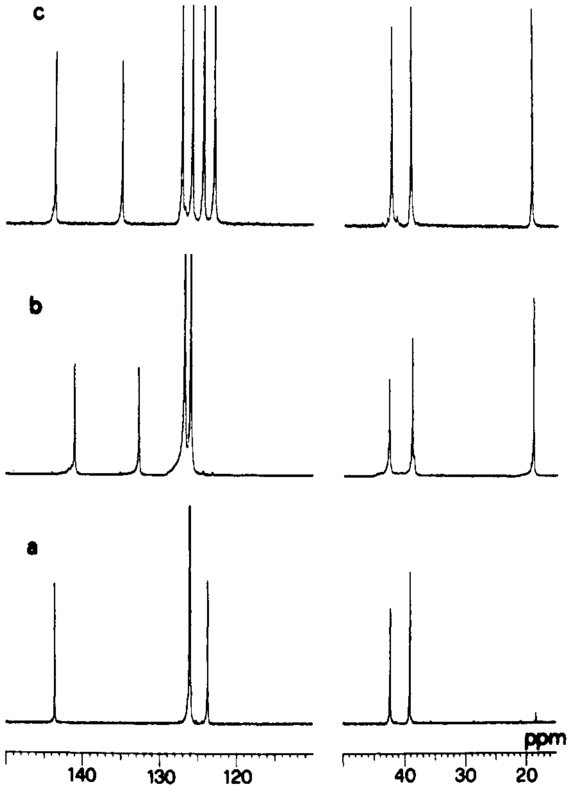

Figure 2. ^{13}C NMR spectra of (a) polystyrene, (b) poly(*p*-methylstyrene), and (c) poly(*m*-methylstyrene). HMDS scale.

The ^{13}C NMR spectra were recorded on a AM 250 Bruker spectrometer operating in FT mode at 62.89 MHz and 393 K. The samples were prepared by dissolving 60 mg of polymer in 0.5 mL of tetrachloro-1,2-dideuterioethane in the presence of hexamethyldisiloxane (HMDS) as internal chemical shift reference. The inverse gated mode of decoupling was used in order to guarantee proportionality of the areas of the signals to the amounts of the corresponding carbon atoms. The compositions of the S–PMS copolymers reported in Table II as *F* (moles of styrene/moles of comonomer) have been evaluated from the ratio of the areas of the signals of the corresponding quaternary carbons C_1 (see Figure 1) of the monomer units. The compositions of the S–PCS copolymers have been evaluated from the areas of the signals of the quaternary carbons C_1 of both S and PCS and that of the chlorine-substituted carbons of PCS.

3. Results and Discussion

Table I reports the results of a series of homopolymerizations of the monomers mentioned in section 1, performed in the same reaction conditions. Due to low conversion, the yields are roughly proportional to the polymerization rates. The polymerization rates appear to decrease in the order PMOS > PMS > S > MMS > PCS > OCS > MCS.

The ^{13}C NMR spectra of polystyrene and of the substituted polystyrenes of Table I are reported in Figures 2 and 3. According to the literature, the presence of single sharp resonances for the quaternary carbons C_1 of polystyrene, poly(*p*-methylstyrene), and poly(*m*-methylstyrene) [respectively at 143.5 ppm (Figure 2a), 140.9 ppm (Figure

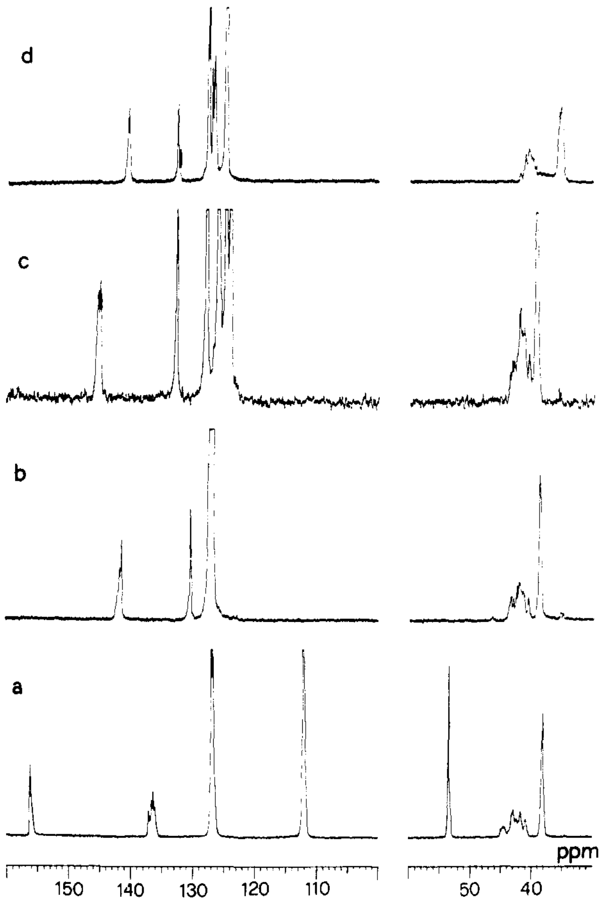

Figure 3. ^{13}C NMR spectra of (a) poly(*p*-methoxystyrene), (b) poly(*p*-chlorostyrene), (c) poly(*m*-chlorostyrene), and (d) poly(*o*-chlorostyrene). The spectra are vertically expanded in order to observe stereoirregularities. HMDS scale.

2b), and 143.6 ppm (Figure 2c)] shows that these polymers are highly syndiotactic.[1] On the contrary, we did not succeed in obtaining highly syndiotactic poly(*p*-methoxystyrene), poly(*p*-chlorostyrene), poly(*m*-chlorostyrene), and poly(*o*-chlorostyrene). In fact, the resonances of the respective quaternary carbons C_1 [centered at 136.3 (Figure 3a), 141.3 (Figure 3b), 144.8 (Figure 3c), and 140.5 ppm (Figure 3d) for the considered polymers] consist of partially resolved multiplets diagnostic of disordered stereochemical environments. The same conclusion can be reached by considering the resonances of the methylene carbons C_6. In fact in the region of the aliphatic carbons of the ^{13}C NMR spectra for polystyrene, poly(*p*-methylstyrene), and poly(*m*-methylstyrene) there are only two sharp resonances respectively at 42.5 and 39.2 ppm for polystyrene, 42.7 and 38.9 ppm for poly(*p*-methylstyrene), and 42.3 and 39.2 ppm for poly(*m*-methylstyrene), which can be easily assigned to methine C_5 and methylene C_6 (see Figure 2) in a highly stereoregular environment. In contrast, in the same region of the spectra reported in Figure 3, one can observe several signals for the methylene carbons C_6 spread in a range from 45.5 to 40.0 ppm for poly(*p*-methoxystyrene), from 44.5 to 40.0 ppm for poly(*p*-chlorostyrene) and for poly(*m*-chlorostyrene), from 43.0 to 37.5 ppm for poly(*o*-chlorostyrene). Binary copolymerizations of S with PMS, PCS, and PMOS were also performed (see Table II). The reactivity ratios, in copolymerization of S with PMS and with PCS (reported in Table III), were evaluated by means of the equation of Fineman and Ross:[9]

$$\frac{1-F}{f} = r_2\frac{F}{f^2} - r_1$$

were F is the composition of the copolymer (molar ratio of styrene to comonomer) and f is the composition of the feed (molar ratio of styrene to comonomer).

Table III
Reactivity Ratios of PMS and PCS in Copolymerization with S

comonomer	r_1[a]	r_2[a]	r_1r_2
PMS	0.55 ± 0.03	2.4 ± 0.1	1.3
PCS	33 ± 3	1.6 ± 0.2	53

[a] By assuming styrene (M_1) and comonomer (M_2). $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ where k_{ij} is the kinetic rate constant for the addition of M_i to a growing chain ending with a M_j monomer unit.

Table IV
Effect of Anisole on Polymerization of S and PMOS

monomer	monomer amt, g	anisole, g	$TiBz_4$,[a] mmol	MAO,[b] g	time, h	yield, mg
PMOS	4.8	0	0	0.200	1	200
PMOS	4.8	1.8	0.025	0.200	1	200
S	4.7	1.2	0.025	0.200	3	~0

[a] Tetrabenzyltitanium. [b] Methylalumoxane.

It is worth noting that polymerization of PMOS occurs even in the presence of methylalumoxane alone and, unlike that of the other monomers, is not inhibited by weak Lewis bases such as anisole. The spectra of the PMOS–S copolymers appear as superposition of the spectra of the two stereoirregular homopolymers (for example, see the spectrum reported in Figure 5). When plotting the copolymer composition against the feed according to the equation of Fineman and Ross a very high value of the r_1r_2 product is obtained. All these facts suggest that in this case there is no copolymerization but rather separate homopolymerization of the two monomers (see later).

Natta and co-workers previously reported a comprehensive investigation concerning the reactivity of substituted styrenes in the presence of heterogeneous isotactic specific catalytic systems.[10] They found, for para-substituted monomers, having, presumably, the same steric hindrance, ideal copolymerization (i.e., $r_1r_2 = 1$) and in addition a reactivity ratio r_1 in the copolymerization of styrene (M_1) with any other monomer (M_2) that was equal to the ratio of the corresponding homopolymerization rates. The reactivity of the investigated monomers followed the Hammet equation with a value of $\rho = -1$.[10] In other words, electron-releasing substituents (I^+) on the aromatic ring increased the reactivity of the monomers while electron-withdrawing substituents (I^-) had a deactivating effect. The reactivity of the growing chain ends was practically independent of the nature of the last added monomer unit.

In the presence of the homogeneous catalyst used by us, only styrene and methyl-substituted styrenes afford syndiotactic homopolymers. The previous observations concerning PMOS suggest that this monomer does not copolymerize with S but rather inhibits syndiotactic homopolymerization of S due to the presence of the methoxy group (see Table III). PCS too shows little tendency to copolymerize with S. The presence of substituents on the aromatic ring not only affects the stereoregularity but also the reactivity of the monomers to a larger extent than Natta and co-workers found.[10] Also in our case the I^+ substituent (CH_3) enhances the monomer reactivity and the I^- substituent (Cl) has the opposite effect, suggesting that the rate-determining step of the insertion is the electrophilic attack of the metal of the catalytic complex to the monomer. The larger influence of the substituents of the aromatic ring can be understood by considering that

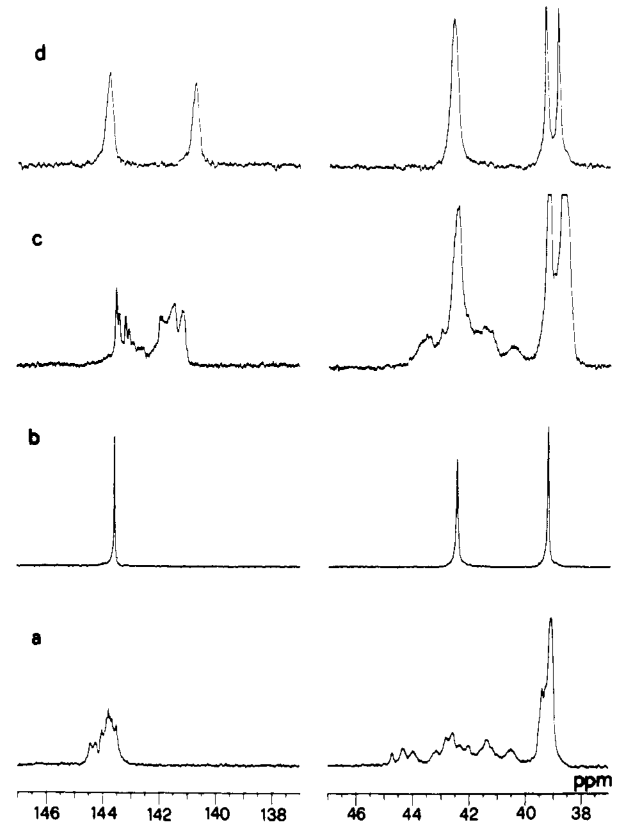

Figure 4. C_1, C_5, and C_6 regions of the ^{13}C NMR spectra of (a) atactic polystyrene, (b) highly syndiotactic polystyrene, (c) the copolymer of styrene with PCS (with $F = 1.1$), and (d) the copolymer of styrene with PMS (with $F = 1.1$).

in our case the polyinsertion of the monomer on the metal–carbon bond of the catalytic complex is secondary[3]

$$\text{M–CH(Ph)CH}_2\text{...} \xrightarrow{+\ \text{PhCH=CH}_2} \text{M–CH(Ph)CH}_2\text{CH(Ph)CH}_2\text{...}$$

while it is primary in isotactic polymerizaton.[11] Of course the electronic effect of the substituent of the ring is transmitted more efficiently to the methine than to methylene carbon. The stereoregularity of polystyrene and poly(methylstyrenes) and the stereoirregularity of poly(chlorostyrenes) may suggest that the aromatic ring of either the monomer or the last unit of the growing chain could be involved in the coordination to the catalyst in order to ensure the syndiotactic steric control. The presence of I^- electron-withdrawing substituents should greatly reduce the coordination of the monomer and (or) of the aromatic ring of the last unit of the growing chain end and, consequently, the stereoregularity of the insertion. In the ^{13}C NMR spectrum of a copolymer of S with PCS (see Figure 4c) one can observe a splitting of the signals corresponding to quaternary carbons C_1 of each monomer. None of the new peaks can be due to a stereoirregular homosequence of styrene (see Figure 4a). The sharp resonances in the region upfield from 143.4 ppm could partially arise from S-centered heterosequences in which the styrene unit experiences a syndiotactic environment. On the other hand, the signals of the carbon C_1 corresponding to the homosequences of PCS and those due to PCS-centered heterosequences appear in the same spectral region downfield from 140.8 ppm. In this region of the ^{13}C NMR spectrum reported in Figure 4c, the peaks are very poorly resolved and this suggests that PCS units should be in a stereoirregular environment. On the contrary, in the spectrum of the copolymer of S and PMS reported in Figure 4d, we can observe only two signals corresponding to quaternary carbons C_1. Although these peaks are comparatively broad, we observe that the corresponding resonances of stereoirregular homopolymers are spread between 143.5 and 145.0 ppm for polystyrene and 140.9 and 141.8 ppm (poly(*p*-methylstyrene)). Therefore it seems reasonable to conclude that the copolymer of S with PMS is cosyndiotactic. This fact seems also to confirm that the

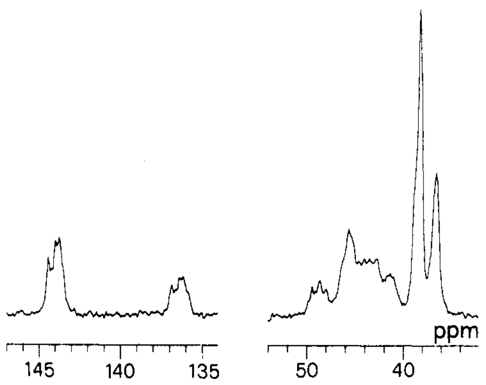

Figure 5. C_1, C_5, and C_6 regions of the ^{13}C NMR spectra of PMOS and S copolymers.

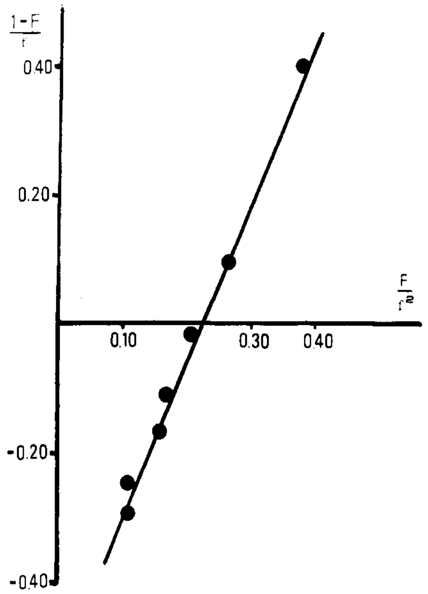

Figure 6. Fineman and Ross plot for the S–PMS copolymers.

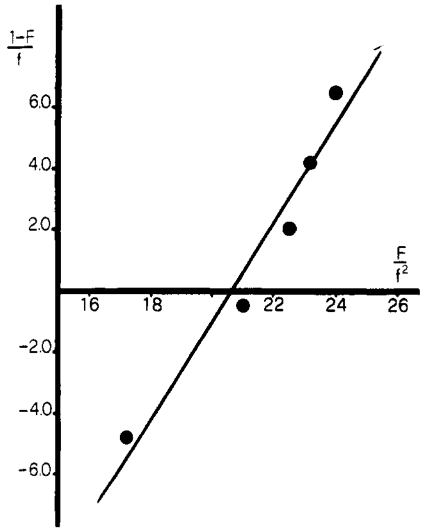

Figure 7. Fineman and Ross plot for the S–PCS copolymers.

coordination of the monomer to the catalytic center is actually determining in the stereoregulation. Poly(*p*-methoxystyrene) is stereoirregular (see Figure 3a). PMOS polymerizes even in the absence of titanium compounds and in the presence of anisole which inhibits syndiotactic polymerization of S. As previously observed S and PMOS do not copolymerize to each other and in the ^{13}C NMR spectrum of this sample (see Figure 5) the quaternary carbons C_1 of S and PMOS are multiplets diagnostic of stereoirregular environments. Probably PMOS polymerizes by a completely different mechanism and deactivates the catalytic complexes syndiotactic specific for styrene polymerization.

Acknowledgment. Financial support by CNR and MPI is gratefully acknowledged.

Registry No. S, 100-42-5; PMS, 622-97-9; MMS, 100-80-1; PMOS, 637-69-4; PCS, 1073-67-2; MCS, 2039-85-2; OCS, 2039-87-4; (S)(MS) (copolymer), 26655-84-5; (S)(CS) (copolymer), 62742-92-1; (S)(MOS) (copolymer), 24936-43-4; anisole, 100-66-3; tetrabenzyltitanium, 17520-19-3; polystyrene, 9003-53-6; poly(*p*-methylstyrene), 24936-41-2; poly(*m*-methylstyrene), 25037-62-1; poly(*p*-methoxystyrene), 24936-44-5; poly(*p*-chlorostyrene), 24991-47-7; poly(*m*-chlorostyrene), 26100-04-9; poly(*o*-chlorostyrene), 26125-41-7.

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Water-Soluble Polymerization Initiators Based on the Thioxanthone Structure: A Spectroscopic and Laser Photolysis Study

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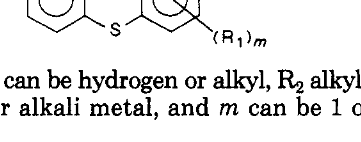
ABSTRACT: This paper reports on the time-resolved and steady-state photochemical study of a new set of water-soluble initiators of polymerization. They exhibit a bell-shaped dependence of the rate of polymerization as a function of the amine concentration. This unusual shape is accounted for by a concurrent quenching of the singlet and triplet states of the initiator by the cosynergist and a pretty good modelization of the polymerization kinetics is achieved. In addition to the study of the initiation ability of these initiators as a function of several chemical parameters, the question of their photochemical properties (fluorescence and triplet quantum yield, quenching constants by electron donnors in the triplet and singlet states, photoreduction quantum yield) is considered with special attention and some structure/reactivity relationships are pointed out.

I. Introduction

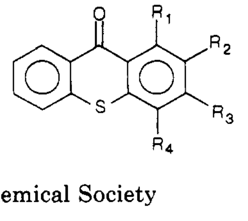
Recently, several types of ketones have acquired importance as photoinitiators of unsaturated hydrocarbon polymerization.[1] The value of some ionic benzophenone and benzil compounds absorbing UV light between 200 and 350 nm has been reported in the literature for the grafting of water-soluble vinylic monomers onto cellulose or wool.[2] Moreover, the high activity of (4-benzoylbenzyl)trimethylammonium chloride or sodium 4-(sulfomethyl)benzophenone for the photopolymerization of acrylamide in aqueous solution,[3] methyl methacrylate in direct lauryl sulfate micelles,[4] or inverse AOT microemulsions[5] was demonstrated.

However, in spite of their high performances, these photoinitiators are only active when irradiated at 365 nm and below in the UV range of the spectrum; therefore, their use in many technical applications which requires illumination in the blue end of the visible spectrum is impossible.

In an effort to overcome these drawbacks, several groups synthesized thioxanthone derivatives that, when used in conjunction with activators, were reported to be specially appropriate for the curing of some coating formulations between 350 and 450 nm. Like in the case of benzophenones or benzils, water-soluble thioxanthones were also developed by introducing ionic substituents in the skeleton of the corresponding oil-soluble compounds. These compounds carry either anionic or cationic solubilizing groups



in which R_1 can be hydrogen or alkyl, R_2 alkylene, M either hydrogen or alkali metal, and *m* can be 1 or 2[6] or



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