side chains of the pure guest component act as a barrier to interaction with the side chains of the host. When donors and acceptors are present in approximately equal numbers and guest and host are not anymore clearly distinguishable, this intraspecies cooperativity is broken and donor-acceptor pairs can be formed with less restriction. It will be noted that the effect is more pronounced in blends of spacer polymers where side-chain interaction in the homopolymer can express itself more freely. It will also be recalled that *p*-methoxycinnamic acid, which is the reactant moiety in P-3-OCH_3, is a well-known mesogen where dipole forces between cinnamoyl groups can lead to liquid crystalline organization.[6]

Conclusions

The decoupling of the functional groups from the polymer backbone does not effectively enhance the photosensitivity of blends of electron donor or acceptor substituted poly(vinyl cinnamates). The dilution effect that accompanies the introduction of spacers into the polymers is more important in determining the concentration of reactive sites than the effect of separating the cinnamoyl groups from the polyvinyl chain. As a result the photoreactivity of the spacer blends is reduced below that of the corresponding nonspacer systems.

The decrease in the number of intermolecular pair sites in blends of spacer polymers is larger than expected for randomly distributed reactants, and this is interpreted as an indication of the partial persistence of the coil structure of the individual polymeric components. This view is also supported by the dependence of the quantum yield of cross-linking on the composition of the blends shown in Figure 7.

In spite of this, the effect of donor-acceptor interactions in the spacer-carrying systems is undeniable. In Figure 4 the quantum yield of cross-linking of the blends is, with one exception, higher than the weighted mean of the quantum yields of the pure components. The fact that donor-acceptor interactions between the reactants are the source of enhanced photosensitivity is further indicated by the effect of casting temperature on quantum yield. The stabilization energy of the donor-acceptor complexes can be derived from these experiments. It is found to be 3.2 and 7.7 kcal/mol, respectively, for the nonspacer and the spacer blends of the Cl- and CH_3O-substituted polymers.

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Triplet-State Reactivity of α-Sulfonyloxy Ketones Used as Polymerization Photoinitiators

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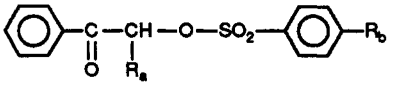
ABSTRACT: Three α-sulfonyloxy ketones have been investigated by laser flash photolysis. The decay kinetics of their triplet states and the radicals formed through β-cleavage and photoreduction were studied, and quenching rate constants by amine, monomer, and hydrogen donor were determined. These data are of interest when these compounds are used as radical or UV-deblockable photoinitiators. A general discussion of the processes involved is presented.

I. Introduction

The present paper is part of a series concerned with the excited-state processes in polymerization photoinitiators[1-7] and the working out of structure-reactivity relationships. Its purpose is to discuss the primary steps involved in the photolysis of α-sulfonyloxy ketones:



1, $R_a = H$; $R_b = CH_3$
2, $R_a = CH_3$; $R_b = CH_3$
3, $R_a = C_6H_5$; $R_b = C_{12}H_{25}$

These compounds[8] as well as α-sulfonylacetophenone **4**,[9] sulfonic acid derivatives of α-hydroxymethylbenzoin **5**,[10] β-sulfonyloxy ketone **6**,[11] *N*-hydroxyimide sulfonates **7**,[12] or quinolinium sulfonates **8**[13] can work as usual radical photoinitiators (except **7** and **8**), but they have been proposed primarily as UV-deblockable and acid-releasing molecules, e.g., for the cross-linking of aminoplast resins[8]

$$\text{blocked photoinitiator in the resin} \xrightarrow{h\nu} \text{acid species} \xrightarrow{\Delta} \text{cross-linking}$$

or the simultaneous activation of radical and acidic cross-linking mechanisms in hybrid systems. In the present investigation, the behavior of **1**-**3** was investigated by time-

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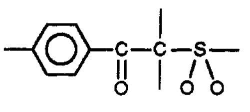

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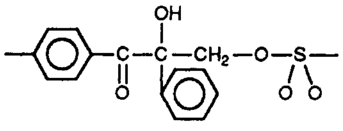

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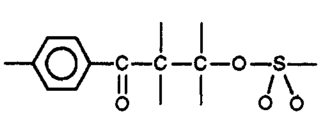

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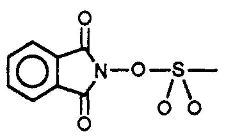

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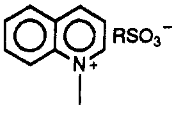

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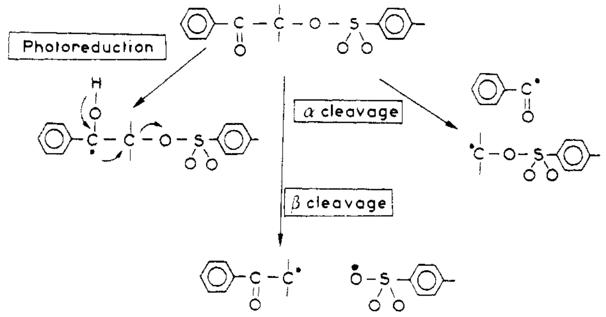
Scheme I



resolved laser spectroscopy in order to determine the efficiency of the radical processes involved.

II. Experimental Section

The photoinitiators were supplied by Ciba Geigy (Basel, Switzerland) as purified laboratory samples. Methyldiethanolamine (MDEA) and methyl methacrylate (MMA) were purchased from Aldrich Chemical Co. and purified as described previously.[5]

The procedure for the photopolymerization experiments has been reported in greater detail elsewhere.[3] The samples are irradiated with a 125-W medium-pressure mercury lamp (λ = 365 nm; $I_0 \approx 5 \times 10^{15}$ photons cm^{-2} s^{-1}).

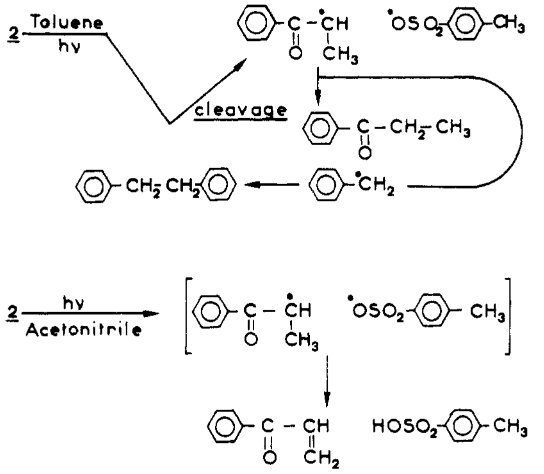
The nanosecond Nd-YAG laser photolysis apparatus used for the investigation of the excited-state processes in real time has been described in ref 4 or 14. The laser source produces a 3-ns pulse (40 mJ) at λ = 353 nm.

III. Results and Discussion

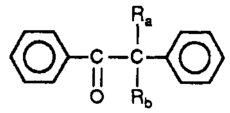
1. Background. Steady-state photolysis of **1**–**3** as investigated by CIDNP[8] results in the formation of products whose processes are interpreted (e.g., Scheme I) on the basis of (i) an α-cleavage side reaction or (ii) a main photochemical reaction involving either β-cleavage and/or photoreduction followed by the elimination of *p*-toluenesulfonic acid, the latter mechanism being considered as the major one.[8]

2. GCMS Experiments. Our GCMS investigation supports the results reported in ref 8 and recalled in the preceding paragraph. For example, while propiophenone is formed during the photolysis of **2** in toluene, the radical pair disappears in acetonitrile medium, mostly through a cage process. This suggests that the radicals are generated through β-cleavage. In hydrogen-donating solvents, photoreduction (as proposed in Scheme I) may also occur (Scheme II) but cannot be substantiated by the present GCMS experiments.

Scheme II

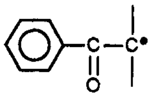


Low yields of benzil were also detected in **1** and **2**, which implies that the α-cleavage producing a benzoyl radical is a minor route of evolution of the excited sulfonyloxy ketones. The yield of benzil is significantly higher in **3**. A more efficient direct α-cleavage suggested by a possible representation of **3** as a phenylacetophenone derivative should probably be considered. For example, this α-cleavage is encountered in benzoin ethers (BE), benzoin (BZ), and **5**:

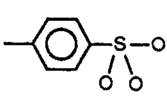


1, R_a = H; R_b = OSO_2-*p*-$C_6H_4C_{12}H_{25}$
BZ, R_a = OH; R_b = H
BE, R_a = OCH_3; R_b = H
5, R_a = OH; R_b = $CH_2OSO_2C_6H_5$

3. Excited-State Processes. A. The β-Cleavage Process. Laser excitation of **1**, **2**, or **3** in acetonitrile reveals the presence of several transients, which absorb weakly in the visible part of the spectrum and decay according to a fast mode and a slow mode (Figure 1). Strong changes in the shape of the overall optical density curve as a function of time, were observed according to the analyzing wavelength used, because of the relative values of the extinction coefficients displayed by the various transient absorptions. In a general way, the primary steps involve—as expected—the fast generation of a short triplet state T_1, which was shown to undergo β-cleavage in toluene or in a non-hydrogen-donating solvent such as acetonitrile (CIDNP and GCMS experiments). This results in the formation of a substituted acetophenyl type radical R_1 and an oxysulfonyl radical R_2:



R_1



R_2

In **1** and **2**, the shorter lived transient at the beginning of the relaxation curves was ascribed to T_1. The quantity $1/\tau_T^0$ (τ_T^0 being the triplet lifetime in a deaerated solution) represents the upper value of the β-cleavage rate constant. In **2**, the triplet-state lifetime is shorter than in **1** (<100 ns). The longer lived transients, responsible for the slow decay in the oscillograms, were attributed to the superposition of R_1 and R_2. For example, the transient absorption spectra of **1** at time t = 0 and t = 1 μs correspond to those of the triplet state and the radicals, respectively (Figure 1). Radical R_1 is known to absorb in the UV or the near-UV-visible region.[15] Similar weak

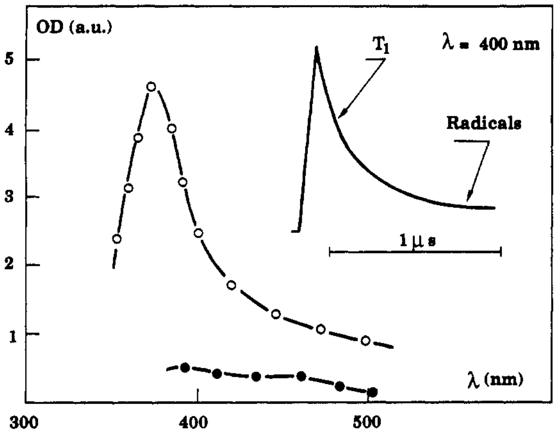


Figure 1. Absorption spectra of the triplet state and the radicals of 1 in degassed acetonitrile.

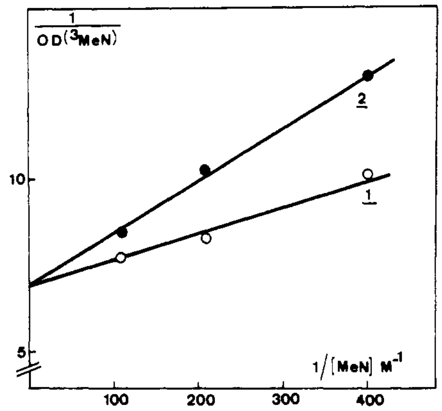


Figure 2. Stern–Volmer plot for the triplet-state quenching by methylnaphthalene at λ = 420 nm.

absorptions in the visible wavelength range were also recorded for sulfonyl,[15b,16a,b] sulfinyl,[16c] and phenyl sulfur radicals.[16c] In the case of 3, the situation is more complex. In 3 absorption of radicals (R_1, R_2, and the benzoyl radical) were superposed in the UV wavelength range according to the β-cleavage process, which should coexist with the α-cleavage detected by GCMS measurements. No triplet-state absorption was clearly detected, as the lifetime is much too short (see below). Oxygen slightly quenches the triplet state of 1. In the presence of air, a new absorption appears (as in hydroxyalkyl ketones,[17] dialkoxyacetophenones,[3] morpholino ketones,[14] and α-hydroxymethylbenzoinsulfonic esters[17]).

B. Quenching by 1-Methylnaphthalene. Quenching by methylnaphthalene (MeN) results in the well-known triplet–triplet absorption of MeN at λ = 420 nm relevant to the energy-transfer process

$$T_1 + \mathrm{MeN} \xrightarrow{k_T} {}^3\mathrm{MeN} + S_0$$

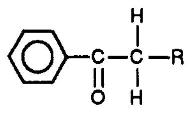
The coefficient $k_T\tau_T{}^0$ and the lifetime of the triplet state $\tau_T{}^0$ in the absence of MeN (if k_T is known) may be derived (Figure 2, Table I) from these experiments according to the double-reciprocal plot (eq 1):

$$\frac{1}{\mathrm{OD}(^3\mathrm{MeN})} = A\left[1 + \frac{1}{k_T\tau_T{}^0}\frac{1}{[\mathrm{MeN}]}\right] \qquad (1)$$

In the case of 1, the quenching of the triplet state by MeN can be followed directly at λ = 400 nm according to

$$\frac{1}{\tau_T} = \frac{1}{\tau_T{}^0} + k_T[\mathrm{MeN}] \qquad (2)$$

(where τ_T is the triplet-state lifetime in the presence of MeN). Such a plot yields $k_T = 5 \times 10^9$ M^{-1} s^{-1}. The data in Table I are self-consistent: combination of $\tau_T{}^0$ and k_T directly measured for 1 yields a Stern–Volmer coefficient $k_T\tau^0$ of 1000 M^{-1}, which is in agreement with the value derived from the data shown in Figure 2. The calculated values of $\tau_T{}^0$ for 2 and 3 displayed in Table I are derived from $k_T\tau_T{}^0$ and k_T (measured for 1). In 3, the shorter lived triplet state observed could reflect the efficiency of the α-cleavage process, competing with the β-cleavage process. These experiments show that β-cleavage occurs through a short triplet state. The electron-donating substituent (CH_3) at the α position in 2 decreases the triplet lifetime, which can be compared with that reported for sulfonyl ketones.[15b] In acetophenyl derivatives, substitution at the α carbon by an oxysulfonyl, sulfonyl, sulfoxide, or sulfide group drastically affects the triplet-state lifetime:



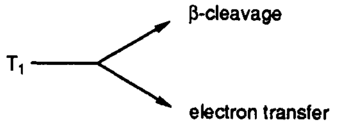
R = OSO_2-*p*-$C_6H_4CH_3$, τ_T = 200 ns
R = $SO_2C_6H_5$, τ_T = 60 ns[15b]
R = SO_2Bu, τ_T = 35 ns[18]
R = SOBu, τ_T = 0.2 ns[18]
R = SBu, τ_T = 0.3 ns[18]

C. Interaction with Amines. Interaction between the triplet states of 1–3 and amines (such as MDEA) results in the quenching of the triplet state; an amine-derived radical and a ketyl type radical are formed through the generation of a charge-transfer complex by electron transfer between the ketone triplet state T_1 and the amine according to

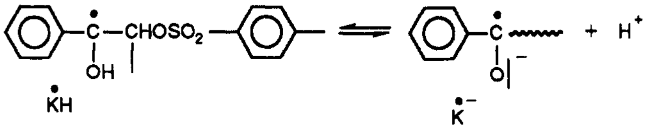
$$T_1 + \mathrm{MDEA} \xrightarrow{k_e} [\text{charge-transfer complex}] \rightarrow \text{radicals}$$

$$\frac{1}{\tau_T} = \frac{1}{\tau_T{}^0} + k_e[\mathrm{MDEA}] \qquad (3)$$

and the concomitant disappearance of radicals R_1 and R_2:



Direct determination with the help of eq 3 leads to $k_e = 3.3 \times 10^9$ M^{-1} s^{-1} for 1 and for 2; 3 is not accurate because of a change in the relaxation curve resulting from an additional new absorption due to ketyl species (ketyl radical and/or ketyl radical anion):



Generation of ketyl species is confirmed when the decay traces are monitored, e.g., at λ = 400 nm. While the radical absorbances decrease as a result of the triplet quenching, the initial overall optical density increases and the relaxation rate constant is changed.

D. The Photoreduction Process. The fast process of β-cleavage observed in a non-hydrogen-donating solvent such as acetonitrile does not preclude the possibility of an efficient competitive process of photoreduction in the presence of a hydrogen donor as suggested in ref 8 and as usually observed in ketones possessing an nπ* triplet state (the values of the rate constant of photoreduction by 2-propanol or THF range from 1 × 10⁶ to 2 × 10⁶ M^{-1} s^{-1} in

Table I
Triplet-State Lifetime in Degassed Acetonitrile (τ_T^0), Rate Constants of MeN Quenching (k_T), Oxygen Deactivation ($k_q^{O_2}$), Electron Transfer (k_e), and Monomer Quenching (k_q), and Stern–Volmer Coefficients ($k_T\tau_T^0$) Calculated from Equation 1 or 2 (See Text)

compd	τ_T^0(measd), ns	$10^{-9}k_T$(eq 2), M^{-1} s^{-1}	$k_T\tau_T^0$(eq 1), M^{-1}	τ_T^0(calcd), ns	$10^{-9}k_q^{O_2}$, M^{-1} s^{-1}	$10^{-9}k_e$, M^{-1} s^{-1}	$10^{-9}k_q$, M^{-1} s^{-1}
1	200	5	930		≤1	3.3	0.25
2			460	90			
3			≤100	≤20			

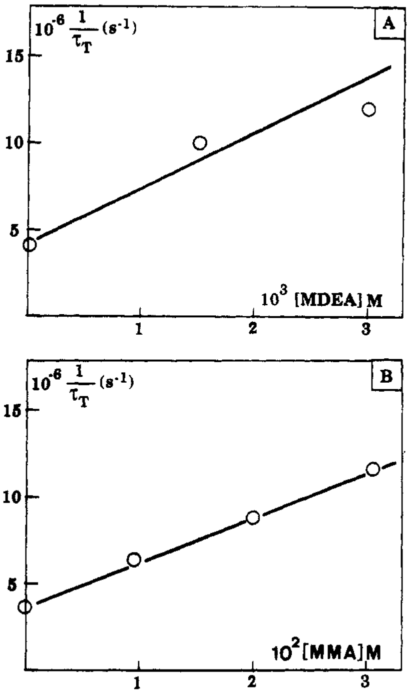
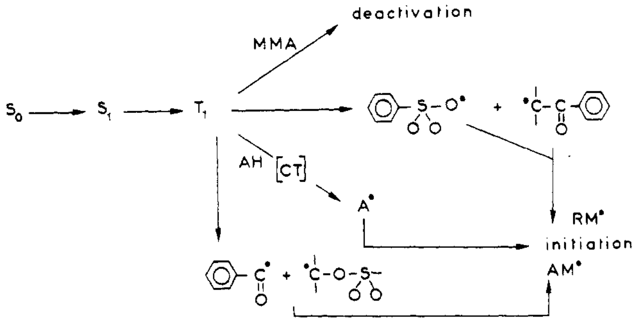
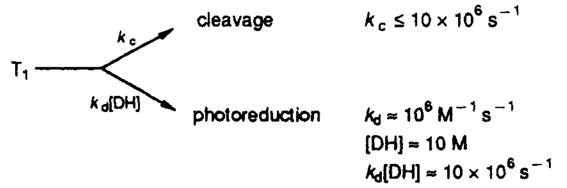


Figure 3. Usual Stern–Volmer plots corresponding to eq 3 (A) and eq 4 (B) (see text).

Scheme III



the benzophenone[19] series). Addition of THF to an acetonitrile solution of **2** shortens the triplet-state lifetime and decreases the radical concentration according to



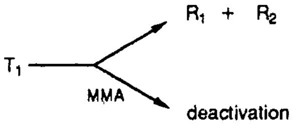
The formation of the long-lived ketyl species is detected as expected. A similar photoreduction process occurs in 2-propanol; in toluene, its contribution is considerably less important. There is no possibility of following clearly in real time the generation (and the relaxation) of R_1, which would have given a definite indication on the ability of the ketyl radical to cleave according to Scheme I. The time scale of evolution of the ketyl radical monitored at λ = 400 nm for **1** in THF (first-order decay with a rate constant $k = 5 \times 10^5$ s^{-1}) is shorter than that usually observed for ketyl type radicals (which disappear according to a second-order kinetics): this result is in agreement with the finding of a cleavage process of the ketyl radical as proposed in Scheme I.[8]

Table II
Relative Rates of Polymerization (R_p) of Methyl Methacrylate (7 M) in Toluene and Computed Quantum Yields ϕ_i, ϕ_β, and ϕ_{CT} (See Text)

	[MDEA] = 0				[MDEA] = 0.05 M		
compd	R_p, au	$\phi_i = R_p^2$, au	ϕ_β	ϕ_{RM}, au	R_p, au	$\phi_i = R_p^2$, au	ϕ_{CT}
1	<1	$<10^{-3}$	0.005		23	0.17	0.1
2	<1	$<10^{-3}$	0.01		13	0.06	
3	5	≤0.01	≤0.05[a]	≤0.2	15	0.07	
DMPA	55	1	1[b]	1		1	
BP					15	0.07	0.2

[a] Overall yields of triplet disappearance including α- and β-cleavage. [b] Quantum yield of α-cleavage. Rate constant of monomer quenching is taken as 2.5×10^8 M^{-1} s^{-1}.

E. Quenching by MMA. When MMA is added to an acetonitrile solution of **1**, **2**, or **3**, both the lifetime of the triplet state and the transient absorption of the radicals decrease as a result of two competitive reactions:



$$\frac{1}{\tau_T} = \frac{1}{\tau_T^0} + k_q[\mathrm{MMA}] \tag{4}$$

A plot according to eq 4 for **1** yields $k_q \approx 2.5 \times 10^8$ M^{-1} s^{-1}. This k_q value corresponds to the usual rate constants of interaction between aryl aryl or aryl alkyl ketones and MMA.[2,3,14,15,16,20]

4. Rates of Polymerization. The general mechanism for the initiation process of the polymerization in toluene is shown in Scheme III. Direct initiation occurs presumably through a reaction between MMA and radicals R_1 and R_2 (and the benzoyl radical in **3**). In the presence of MDEA, amine-derived radicals are formed through the quenching of the triplet state by electron transfer followed by a proton transfer (the ketyl structure that is formed in this process may cleave, as discussed in section 3D, and lead to the production of an acetophenyl radical). Quantum yields of initiation (ϕ_i), cleavage (ϕ_β) and electron transfer (ϕ_{CT}) are computed in Table II.

$$R_p = K\phi_i^{1/2}$$

$$\phi_\beta = \frac{k_\beta}{k_\beta + k_q[\mathrm{M}]}$$

$$\phi_{CT} = \frac{k_e[\mathrm{AH}]}{k_\beta + k_e[\mathrm{AH}] + k_q[\mathrm{M}]}$$

where k_β, k_e, and k_q are the rate constants of β-cleavage, electron transfer with amine (AH), and monomer quenching (M). According to the very low values calculated for the different processes, sulfonyloxy ketones are rather poor radical photoinitiators in the absence of amine (comparative data for (2,2-dimethoxyphenyl)acetophenone (DMPA) and benzophenone (BP) are listed in Table II). On the other hand, these ketones are efficient sources of latent sulfonic acids,[8] because of the high reactivity of their triplet states (k_β, k_e, k_d) in the absence of acrylic monomers.

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Polymerization of Monomers Containing Functional Silyl Groups. 8. Catalytic Hydrogenation of Poly(2-silyl-substituted-1,3-butadiene)s

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ABSTRACT: Catalytic hydrogenation of five poly(2-silyl-substituted-1,3-butadiene)s and block copolymers containing silyl functions was carried out under various conditions. The polymers were allowed to react with hydrogen at an initial pressure of 80 atm in cyclohexane at 110 °C for 5 h in the presence of palladium on carbon, leading to quantitative saturation of the double bonds regardless of the substituent on silicon atom. Molecular weights and the molar ratio of catalyst to double bonds influence the degree of hydrogenation (DH). The higher molecular weight lowers the DH. Wilkinson's complex, $Rh(PPh_3)_3Cl$, showed no activity for the hydrogenation of *cis*-1,4-poly[2-(triisopropoxysilyl)-1,3-butadiene] whereas it was effective for *cis*-1,4-polyisoprene and dangling vinyl groups in other silyl-substituted polydienes.

Introduction

Polyolefins such as polyethylene and polypropylene are well-known commodity polymers and are used in many fields. In many cases, they are produced by free-radical polymerization or coordination polymerization with a Ziegler type catalyst. Because the polymerization mechanisms include transfer and termination reactions, polyolefins and block copolymers with polyolefin segments can have branched structures and broad distribution of molecular weights. To obtain polyolefins and the block copolymers with controlled chain structures, polydienes and the block copolymers produced by anionic living polymerization are hydrogenated under suitable conditions to be converted to polyolefins without losing their original characteristics such as molecular weight, molecular weight distribution, and microstructure. Many authors have reported the preparation of tailor-made polyolefins by this method.[1] Since the molecular weight, molecular weight distribution, and the structure of the repeating unit in the resulting polyolefins can be precisely controlled by the polymerization condition of the original 1,3-dienes, this relatively complicated synthetic method is still attractive both in academic and industrial fields. Poly(ethylene-*alt*-propylene), poly(ethylethylene), and atactic polypropylene with a narrow molecular weight distribution were synthesized[2] by hydrogenation of 1,4-polyisoprene, 1,2-polybutadiene, and poly(2-methyl-1,3-pentadiene), respectively. The solution properties of these polymers such as characteristic ratio and temperature coefficients of unperturbed dimensions were studied. Polyethylene–poly(1-butene) block copolymer derived from 1,4-polybutadiene–1,2-polybutadiene block copolymers can be used as thermoplastic elastomers.[3] When the poly[styrene-

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