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Cationic Polymerization of Isobutyl Vinyl Ether: Livingness Enhancement by Dialkyl Sulfides[†]

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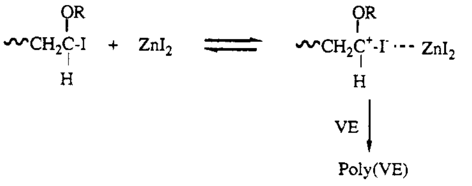
ABSTRACT: The synthesis of well-defined living polymers of isobutyl vinyl ether (IBVE) has been accomplished with trifluoromethanesulfonic (triflic) acid or Lewis acids plus proton sources as initiators. Excess alkyl sulfides were used to stabilize the carbocationic chain ends. The number-average molecular weight (M_n) of the polymers obtained was directly proportional to monomer conversion. The molecular weight distribution (MWD) was narrow. As the sulfide concentration was increased, the rate of polymerization decreased and a nearly monodisperse polymer was obtained. With triflic acid initiator living conditions were observed at −40 and −15 °C. With $EtAlCl_2$ initiator the living polymer is obtained even at 0 °C. When the bulkiness of the sulfide was increased, the rate of polymerization increased but the system deviated from living behavior. Mechanistic studies indicate that alkyl sulfides reduce the concentration of active propagating species via reversible sulfonium ion formation.

Introduction

In recent years there has been much interest in the development of living cationic polymerization techniques for the synthesis of well-defined polymer structures. To obtain stable active chain ends for living cationic polymerization, one must eliminate chain transfer and termination. This can be accomplished by formation of covalent species from the growing carbocation chain ends capable of inserting a monomer or by regenerating carbocations reversibly at low concentration.[1] Between these extremes, stabilization by ion pairing and/or charge-transfer complexation remain possibilities. It is becoming apparent that each monomer will require its own special set of initiators to obtain living polymerizations. In this work we describe a set of conditions for the living polymerization of vinyl ethers and kinetic studies relative to the chain propagation mechanism.

Higashimura et al.[2,3] have reported two general cationic systems each with subvariations for polymerization of vinyl ethers. In the first method a small amount of active carbocationic propagating species is formed in equilibrium with a labile covalent end group. For example an α-iodo ether ended polymer is activated for monomer insertion by iodine or ZnI_2 (eq 1). A similar example is the living polymerization of isobutylene with an acetate counterion.[4] In the second method[5-7] a Lewis base (LB), e.g., dioxane or ethyl acetate, is used to stabilize the carbocation generated by the reaction of the monomer with a proton source, e.g., $H_2O/EtAlCl_2$ or $CH_3CO_2H/EtAlCl_2$. An oxonium ion, 1, or a solvated carbocation, 2, have been proposed as the reactive species (eq 2).



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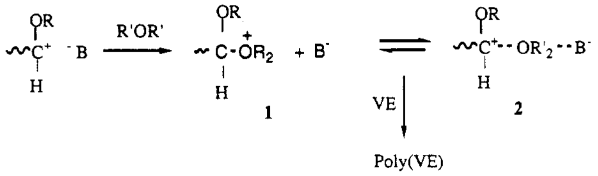

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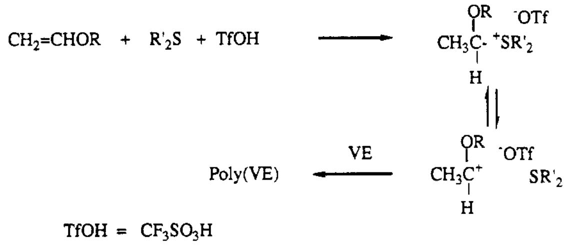
For both the above methods, only minor efforts[1,8,9] have been made to elucidate the reaction mechanism. Instead, efforts have mainly focused on the discovery of new living initiating systems.[10,11] Zsuga and Kelen[12] have introduced the hard and soft acid and base (HSAB) principle[13] to explain the living behavior in their phosgene-stabilized isobutylene polymerization system. We have used alkyl sulfides as LB's to achieve controlled polymerization of isobutyl vinyl ether (IBVE) and used triflic acid as the initiator (eq 3). The effect of structure and concentration of sulfides on the rate of polymerization was studied.



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Experimental Section

Materials. IBVE and ethyl vinyl ether (EVE) (both from Aldrich) were purified as reported previously.[9] *n*-Hexane (Baker, HPLC grade) was also treated as reported previously and distilled over sodium–potassium alloy under dry argon. Methylene chloride (EM Science) was treated with concentrated sulfuric acid and then fractionally distilled successively over phosphorus pentoxide and calcium hydride under dry argon. Triflic acid (Fluka) was distilled by the trap to trap method and was stored as a methylene chloride solution. Doubly distilled methylene chloride was further purified over a sodium mirror for

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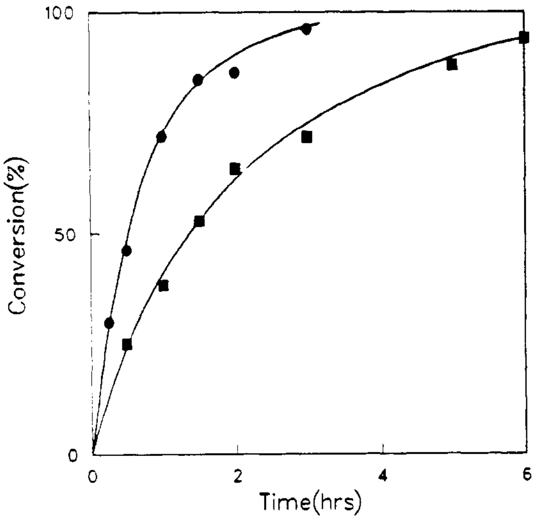


Figure 1. Time–conversion curves of IBVE polymerization at -40 °C in methylene chloride ($[IBVE]_0$ = 0.76 M (10 vol %); $[TfOH]_0$ = 8.6 mM; $[LB]_0/[TfOH]_0$ = 30): (■) dimethyl sulfide; (●) tetrahydrothiophene.

this purpose. For a normality determination, the solution was extracted with distilled water and then titrated with a 0.1 N sodium hydroxide solution with phenolphthalein indicator. Dimethyl sulfide and tetrahydrothiophene (both from Aldrich) were distilled over either sodium metal or 9-borabicyclo[3.3.1]nonane. Other sulfides were obtained from available commercial sources and fractionally distilled over calcium hydride. Ethylaluminum dichloride (1.0 M solution in hexane) and boron trifluoride etherate (from Aldrich) were used as received. Other chemicals were obtained from various commercial sources and used after purification.[14]

Procedures. The polymerizations were carried out in a flask equipped with a modified two-way Teflon stopcock in a bath. The bath temperature was controlled by an immersion cooler (within ±1 °C). The polymerizations were started by injecting the triflic acid solution into the monomer/sulfide charge. The reaction time was counted from the moment when the acid solution was injected. After a given time the polymerization was quenched by injecting 10 mL of *tert*-butyl amine/methanol (1/2 v/v) solution. The unreacted monomer and solvent in the quenched reaction mixture were removed by rotary evaporation. The polymer mixture was dried under vacuum (1 Torr) at ca. 40 °C for 2 days, and the yield was measured by gravimetry.

The molecular weights and MWD's of the polymers were determined by gel permeation chromatography (GPC) with poly(methyl methacrylate) standards. M_n was also obtained by vapor phase osmometry (VPO). The proton NMR spectra were recorded on a 300-MHz GE NMR spectrometer.

Results and Discussion

Demonstration of Living Polymerization. Figure 1 shows the kinetic curves of the polymerization of IBVE at -40 °C in methylene chloride. The polymerization was initiated by adding a triflic acid solution to a solution of IBVE containing either dimethyl sulfide or tetrahydrothiophene. No induction period was observed, and the polymerization mixture remained completely colorless and homogeneous throughout the reaction. It appears that the addition of triflic acid to the monomer in the presence of an alkyl sulfide is instantaneous and generates sulfonium triflate (Scheme I). The reactivity of the monomeric sulfonium ion is expected to be similar to those of the polymeric homologues. A change in the addition sequence to generate the sulfonium triflate first, did not affect the outcome of the polymerization.

The -ln (1 - conversion) versus time plot shows a first-order rate dependence on the monomer concentration. This relationship held even for conditions that gave a polymer with a broad molecular weight distribution, indicating that the dominant side reaction is proton transfer to the monomer.[15,16]

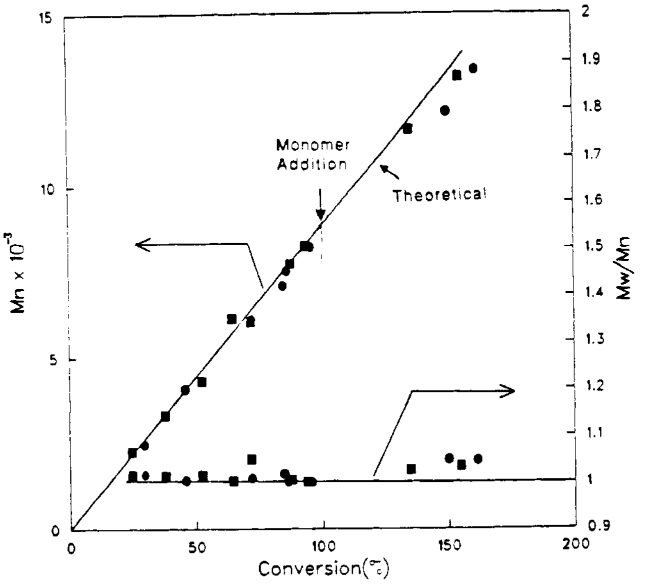


Figure 2. Conversion–M_n plot of poly(IBVE) obtained at -40 °C in methylene chloride $[IBVE]_0$ = 0.76 M (10 vol %); $[TfOH]_0$ = 8.6 mM; $[LB]_0/[TfOH]_0$ = 30): (■) dimethyl sulfide; (●) tetrahydrothiophene.

Scheme I
Initiation

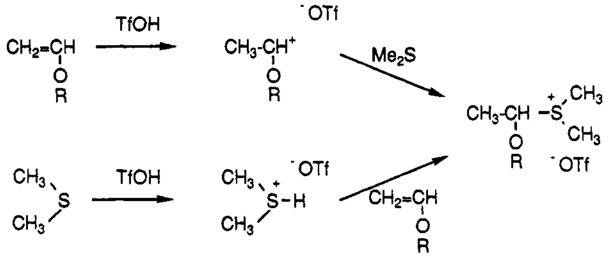


Figure 2 shows the M_n and polydispersity ratios (M_w/M_n) of the polymers obtained. The M_n values are directly proportional to monomer conversion and are in excellent agreement with calculated values assuming that one triflic acid molecule forms one polymer chain. The M_n by VPO closely matched that obtained by GPC.

When a fresh feed of IBVE (0.76 M, equivalent to the first charge) was added to the completely polymerized reaction mixture, polymerization resumed at nearly the same rate as in the first stage. M_n values increased in proportion to conversion and were in good agreement with calculated values. The rate of polymerization was greater with tetrahydrothiophene than with dimethyl sulfide as LB. The MWDs were slightly broadened by sequential addition but were still very narrow (M_w/M_n < 1.05).

At higher temperatures the rate of polymerization was greater and more alkyl sulfide was needed for control. With dimethyl sulfide as a solvent (Table I), good molecular weight control was obtained at -15 °C. At 0 °C, with triflic acid initiator, the living nature of the polymerization began to fail. By using BF_3/H_2O or $EtAlCl_2/H_2O$ as proton sources,[17] one can maintain livingness to 0 °C (Table I). These results show that the nucleophilicity of the counterion as well as the ratio of LB to active propagating species affects the livingness of the system.

Role of Lewis Base. Table II shows the effect of di-

Table I
Polymerization of IBVE in Me_2S Solvent[a]

initiator	solv[b]	temp, °C	time, h	% conv	M_w/M_n	M_n[f] (GPC)
TfOH[c]	Me_2S	-15	4	60	1.16	3800
TfOH[c]	Me_2S	0	1	95	1.68	2870
TfOH[c]	Me_2S/*n*-hex (1/2)	0	2	quant	2.30	2080
$EtAlCl_2$[d]	Me_2S	0	2	quant	1.10	4990
$EtAlCl_2$[d]	Me_2S/*n*-hex (1/1)	0	2	quant	1.12	3370
$EtAlCl_2$[e]	*n*-hex	0	3	quant	1.19	35400

[a] $[IBVE]_0 = 0.76$ M. [b] Volume ratio in parentheses. [c] $[TfOH]_0 = 8.6$ mM. [d] $[EtAlCl]_0 = 31$ mM; $[PhCHO]_0 = 8.5$ mM. [e] $[EtAlCl] = 20$ mM; no aldehyde; $[Me_2S]_0 = 0.26$ M. [f] Theory $M_n = 8800$ for quantitative conversion (except in last example).

Table II
Effect of $[Me_2S]_0/[TfOH]_0$ on Conversion of IBVE Polymerization at -40 °C in Methylene Chloride[a]

			M_n	
$[Me_2S]_0$	% convn	M_w/M_n	GPC	theory
0	quant	8.51	11800	8800
2	quant	1.50	5040	8800
4	94.4	1.36	5470	8300
5	95.1	1.60	4860	8400
7	74.7	1.37	4560	6600
10	67.2	1.17	5240	5900
15	42.5	1.19	2970	3700
30	25.0	1.02	2250	2200

[a] $[IbVE]_0 = 0.76$ M (10 vol %); $[TfOH]_0 = 8.6$ mM; reaction time = 30 min.

methyl sulfide concentration on the rate of polymerization and polydispersity. As the concentration increased, the MWD became narrower and the rate of polymerization decreased. A similar phenomenon was observed by Higashimura et al.[5,18] in the polymerization of IBVE, stabilized by ethers, esters, or hindered amines.

In order to check the possibility of sulfonium ion formation, 1 equiv of triflic acid was added to 2 equiv of dimethyl sulfide in deuterated methylene chloride, and then 1 equiv of EVE was added. Proton NMR spectra of the mixture at different temperatures are shown in Figure 3. At -50 °C two separate methyl peaks (2.7, -2.8 ppm) from the dimethylsulfonium ion were observed, and the excess dimethyl sulfide showed a single peak at ~2.0 ppm. At -30 °C this observation did not change much, but at 0 °C the three peaks became quite broad. The rate of polymerization at -30 °C is much faster than that at -50 °C with an initial $[Me_2S]/[TfOH]$ ratio of 30. At 0 °C under the same conditions the polymerization is not living.

Figure 3 clearly shows that dimethyl sulfide reacts with the carbocation and generates a carbon–sulfur bond at low temperature. As the temperature increases, the bond strength decreases and fast exchange occurs. Two kinds of exchanges are possible: (1) internal exchange that may occur by breaking of the carbon–sulfur bond, i.e., the dimethyl sulfide in a sulfonium ion may undergo dissociation and collapse and (2) external exchange that may occur between the sulfonium ion and an external sulfide by S_N2 attack.

A possible chain propagation mechanism (Scheme II) is as follows: (1) a carbocation propagates until captured by dimethyl sulfide and becomes a sulfonium ion; (2) the sulfonium ion forms a carbocation by reversible equilibrium or undergoes nucleophilic attack by the monomer; (3) repetition of steps 1 and 2; (4) the sulfonium ion may undergo exchange with dimethyl sulfide, but this does not influence the polymerization.

Depending on the relative ratios of k_1, k_2, k_p, and k_p' the polymerization path will be different. Three possibilities exist depending on k_2/k_p': (1) $k_2 \gg k_p'$, the case when the carbocation is generated by a reversible equilibrium reaction; (2) $k_2 \ll k_p'$, the case when the sulfonium ion undergoes S_N2 by monomer; (3) $k_2 \sim k_p'$, the case where both paths are followed. The data in Table II can be tested for each case. If $k_1 \gg k_2$ and $k_1 \gg k_p'$, then $[S^+] \sim [TfOH]_0$. $[R_2S] \sim [R_2S]_0 - [TfOH]_0$ when $[R_2S]_0/[TfOH]_0 > 1$.

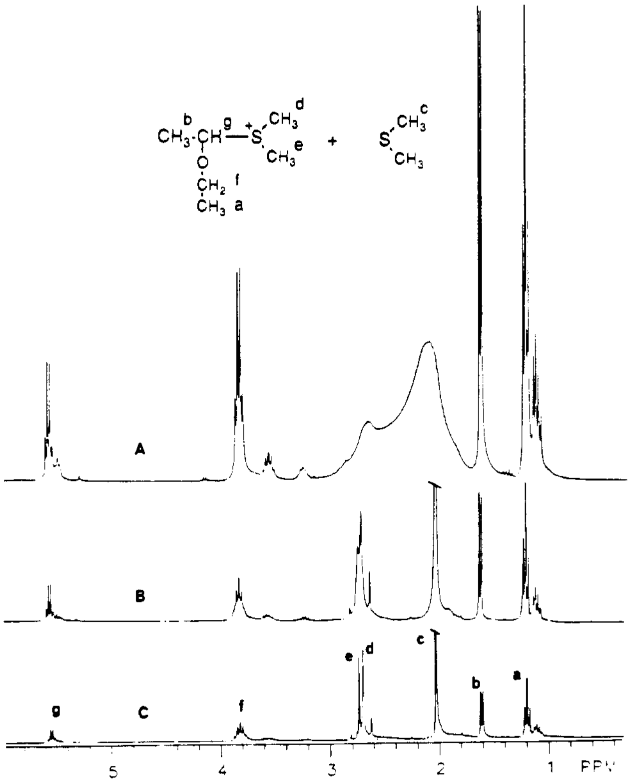
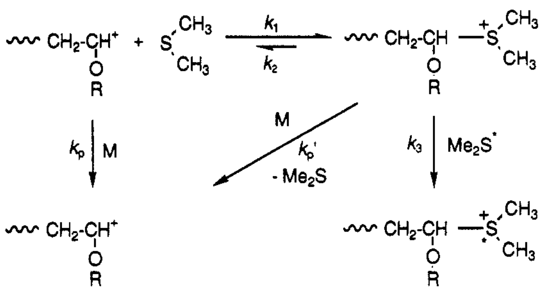


Figure 3. Proton NMR spectra of EVE + TfOH + Me_2S in CD_2Cl_2 ($[EVE]_0 = 0.54$ M; $[TfOH]_0 = 0.54$ M; $[Me_2S]_0 = 1.1$ M): (A) 0 °C; (B) -30 °C; (C) -50 °C.

Scheme II
Propagation



Case 1, $k_2 \gg k_p'$. If both the carbocation and the sulfonium ion are involved in propagation, the overall rate of polymerization (R_p) is the sum of the propagation rates:

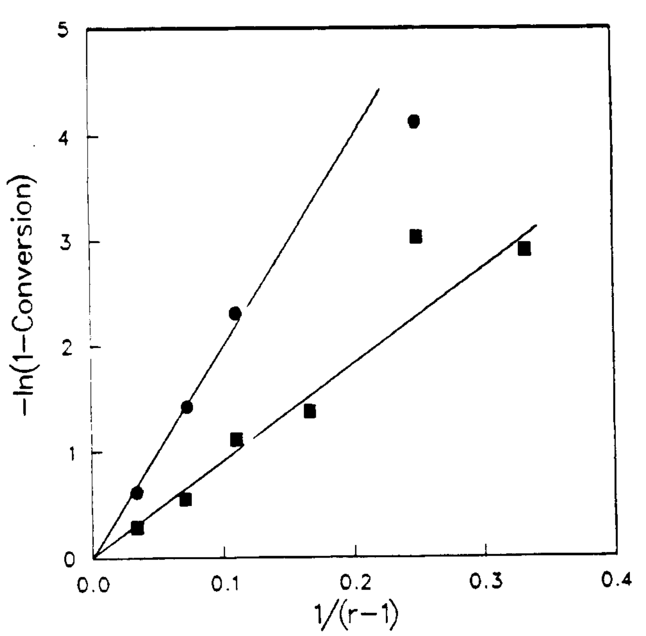


Figure 4. Effect of LB concentration on the conversion of IBVE polymerization at −40 °C in methylene chloride ($[\mathrm{IBVE}]_0 = 0.76$ M (10 vol %); $[\mathrm{TfOH}]_0 = 8.6$ mM; reaction time = 30 min; $r = [\mathrm{LB}]_0/[\mathrm{TfOH}]_0$): (■) dimethyl sulfide; (●) tetrahydrothiophene.

$$\begin{aligned} R_p &= -\mathrm{d}[\mathrm{M}]/\mathrm{d}t \\ &= k_p[\mathrm{C}^+][\mathrm{M}] + k_p'[\mathrm{S}^+][\mathrm{M}] \end{aligned}$$

After substitution and rearrangement

$$\begin{aligned} R_p &= \{k_p[\mathrm{TfOH}]_0/\{K_{eq}([\mathrm{R_2S}]_0 - [\mathrm{TfOH}]_0)\} + k_p'[\mathrm{TfOH}]_0\}[\mathrm{M}] \\ &= \{k_p/K_{eq}(r-1) + k_p'[\mathrm{TfOH}]_0\}[\mathrm{M}] \end{aligned}$$

where $r = [\mathrm{R_2S}]_0/[\mathrm{TfOH}]_0$, the initial ratio of alkyl sulfide to triflic acid, and $K_{eq} = k_1/k_2$, the equilibrium constant. By integration from time zero to time t

$$-\ln(1 - \text{conversion}) = k_p/K_{eq}(r-1)t + k_p'[\mathrm{TfOH}]_0 t$$

This equation predicts that a plot of $-\ln(1 - \text{conversion})$ versus $1/(r-1)$ at a certain time t will be linear with a slope of k_p/K_{eq} and intercept of $k_p'[\mathrm{TfOH}]_0$. The plot of data in Table II indeed shows a linear relationship (Figure 4). The deviation at higher conversions originates from experimental error inherent in yield measurements. A similar result was obtained with tetrahydrothiophene. In both cases the lines converge to zero as the amount of sulfide increases, implying that the $k_p'[\mathrm{TfOH}]_0$ is zero. K_{eq} can be approximated as 10^4–10^5 from the slope in Figure 4 and from the reported value of the rate constant for IBVE polymerization.[15]

The above equation shows that r is the most important factor for the kinetics, and the contribution of the initial acid concentration is quite small. The data in Table III show that the conversion did not increase by an increase in acid concentration with r constant rather it showed a slight decrease. M_n values were in excellent agreement with theoretical values, and MWDs stayed quite narrow even though the acid concentration changed more than ten times.

Case 2, $k_2 \ll k_p'$. The overall rate of polymerization is

$$\begin{aligned} R_p &= -\mathrm{d}[\mathrm{M}]/\mathrm{d}t \\ &= k_p[\mathrm{C}^+][\mathrm{M}] + k_p'[\mathrm{S}^+][\mathrm{M}] \\ &= k_p k_p'[\mathrm{S}^+][\mathrm{M}]^2/(k_1[\mathrm{R_2S}]) + k_p'[\mathrm{S}^+][\mathrm{M}] \end{aligned}$$

Table III
Effect of Initial Triflic Acid Concentration on the Conversion of IBVE Polymerization[a]

$[\mathrm{TfOH}]_0$, mM	% convn	M_w/M_n	M_n GPC	M_n theory
1.10	69.6	1.10	40400	48400
2.17	65.6	1.06	23100	23200
4.34	65.9	1.01	11400	11700
8.67	64.1	1.05	5250	5700
13.0	62.5	1.01	3330	3700
17.3	61.1	1.07	2200	2700

[a] $[\mathrm{Me_2S}]_0/[\mathrm{TfOH}]_0 = 30$; $[\mathrm{IBVE}]_0 = 0.76$ M (10 vol %); temp = −40 °C; solvent = $\mathrm{CH_2Cl_2}$; reaction time = 2 h.

Table IV
Effect of Initial Monomer Concentration on Polymer Conversion[a]

IBVE, vol %	% convn after 2 h	M_w/M_n	M_n GPC	M_n theory
10	64.1	1.05	5250	5700
20	63.7	1.00	11500	11300
30	69.0	1.05	18100	18300

[a] $[\mathrm{Me_2S}]_0/[\mathrm{TfOH}]_0 = 30$; $[\mathrm{TfOH}]_0 = 8.6$ mM; temp = −40 °C; solvent = $\mathrm{CH_2Cl_2}$.

After substitution and rearrangement

$$\{1/[\mathrm{M}] - 1/([\mathrm{M}] + k_1[\mathrm{R_2S}]/k_p)\}\mathrm{d}[\mathrm{M}] = -k_p'[\mathrm{S}^+]\mathrm{d}t$$

By integration from time zero to time t

$$\text{conversion}/(1 - \text{conversion}) \sim 1/(r-1) \quad \text{when } k_1[\mathrm{R_2S}] \ll k_p[\mathrm{M}]$$

where $r = [\mathrm{R_2S}]_0/[\mathrm{TfOH}]_0$, and

$$-\ln(1 - \text{conversion}) \sim k_p'[\mathrm{TfOH}]_0 \quad \text{when } k_1[\mathrm{R_2S}] > k_p[\mathrm{M}]$$

The above equations do not fit the data in Tables II and III, and a similar result is obtained when $k_1[\mathrm{R_2S}] \sim k_p[\mathrm{M}]$. Therefore the assumption that $k_2 \ll k_p'$ is not true.

Case 3, $k_2 \sim k_p'$. When $k_2 \sim k_p'$, more polymer will be formed via carbocationic propagation than by the $\mathrm{S_N2}$ route because $k_p > k_p'$, and it will converge to case 1.

The data in Table III confirm that k_p' is negligible; i.e., the sulfonium ion is not responsible for chain propagation. The data in Table IV show the influence of the initial monomer concentration on the rate. For all concentrations, conversions were in the same range, indicating that the above-mentioned rate equation in case 1 is valid.

The data in Table V show the effect of the size of the sulfide alkyl groups on the rate of polymerization, molecular weight control, and polydispersity. The rate of polymerization was slowest with dimethyl sulfide as LB. The polymerization proceeded at about the same rate in the presence of ethyl, *n*-propyl, and *n*-butyl sulfides. Bulky sulfides such as di-*tert*-butyl did not enhance the longevity of vinyl ether polymerizations. Polymerization mixtures with bulky sulfides were yellow to black depending on the bulkiness of the sulfide. The color of the polymerization mixture with *tert*-butyl sulfide as LB was as dark as that of runs without added base.[19] In the initiation stage, added triflic acid may make protonated sulfonium ion first, and the proton-transfer step to the monomer for the initiation reaction may be retarded by the bulkiness of the sulfonium ion, contributing to the broad-

Table V
Size Effect of Alkyl Sulfide[a]

sulfide	% convn	M_w/M_n	M_n GPC	M_n theory
Me_2S	8	1.20	585	720
Et_2S	67	1.00	5530	5900
n-Pr_2S	75	1.04	6180	6600
i-Pr_2S	quant	3.49	7970	8900
n-Bu_2S	69	1.07	5180	6100
i-Bu_2S	quant	1.02	8590	8900
Me(*t*-Bu)S	quant	1.55	5870	8900
sec-Bu_2S	quant	3.22	7210	8900
t-Bu_2S	quant	8.52	11700	8900
[b]	quant	24.1	10600	8900

[a] $[Sulfide]_0/[TfOH]_0 = 30$; $[IBVE]_0 = 0.76$ M (10 vol %); $[TfOH]_0 = 8.6$ mM; temp = −50 °C; solvent = CH_2Cl_2; reaction time = 1 h. [b] No sulfide.

ening of the MWD. This contribution must be small because a narrow MWD would still be obtained if the remaining sulfide reacts strongly with the growing carbocation, slowing down the rate of propagation. With linear alkyl as well as isobutyl sulfides, the polymer with excellent molecular weight control and narrow dispersity was obtained.

These data clearly show that the sulfide is involved in an equilibrium reaction involving the carbocation and the sulfonium ion during the polymerization. As the bulkiness of the sulfide increases, the formation of the covalent sulfonium ion becomes more difficult due to steric hindrance, and therefore more carbocations will be available for propagation. The observation that the rate of polymerization of methyl vinyl ether was several times slower than that of IBVE in the presence of dimethyl sulfide also supports this interpretation.

The proposition that the sulfonium ion is inactive is similar to that proposed by Subira et al.[20] for the nonliving polymerization of alkyl vinyl ethers initiated by trityl hexachloroantimonate in methylene chloride without added LB. They described the propagation with three different species: i.e., bare ion, solvated ion, and polymeric ether solvated ion in equilibrium. Among these, the polymeric ether solvated ion was believed to be inactive. In our study, the sulfide is also involved in the equilibrium and reacts strongly with growing chain ends. The resulting sulfonium ion, however, cannot be responsible for propagation since excess sulfide decreases the rate of polymerization. A similar interpretation can be applied to the system of Higashimura[5] et al., where the carbocation is stabilized by an ether. Moreover, the retarding effect of excess sulfide demands that a sulfide complexed species of any kind cannot be responsible for chain growth. (The amount of sulfide complex would not be lowered by the addition of excess sulfide.) One must conclude then that the same species leads to propagation in the presence of a sulfide as in the absence of a sulfide. However, its *concentration* is greatly reduced when the sulfide is present. This species could be a triflate, an ion pair, or a solvated ion. Since BF_3 or $EAlCl_2$ in combination with a carbenium ion source operates as well as triflic acid for initiation, we feel a covalent species is unlikely. One is left, therefore, to explain why a very low steady-state concentration of ionic living ends, solvated or as ion pairs, is more stable (less chain transfer and termination) than a higher concentration of the same ions during living polymerization. There are at least two possible explanations: (1) chain transfer and/or termination could be occurring by a first-order process that is slowed down more than the second-order propagation process when the reactive species concentration is lowered or (2) the monomer is forming a charge-transfer complex with the reactive chain ends. The equilibrium would be shifted in favor of the C–T complex by lowering the concentration of the reactive species. This proposal requires that the C–T be stable to chain transfer but not retard polymerization. Szwarc et al. noted that the presence of the monomer appears to stabilize cationic polymerizations.[22] Carbenium ion/monomer complexes have been proposed by Plesch as the explanation for the stabilizing effect of monomers on living cationic polymerizations.[23]

Conclusions

The use of an alkyl sulfide and a strong proton source allows one to obtain a living polymer from isobutyl vinyl ether by suppressing chain-transfer reactions. The polymerization rate becomes slower and the polydispersity of the polymers becomes narrower as the bulkiness of the alkyl sulfide decreases and as the concentration of the alkyl sulfide increases. The rate of polymerization depends mainly on the initial ratio of the alkyl sulfide to triflic acid.

The alkyl sulfide reduces the concentration of the carbocation via formation of a sulfonium ion. A fast equilibrium between the carbocation and the sulfonium ion explains the observed polymerization phenomena. During the polymerization, the major portion of the growing chain ends exists as a sulfonium salt and only a small portion of the growing chain ends will be carbocations. The sulfonium ion itself is inactive but dissociates into a carbocation for propagation and quickly collapses to the sulfonium ion.

Acknowledgment. We thank to Dr. M. Han for GPC measurement and to Dr. F. Davidson for suggestions and NMR measurements. We gratefully acknowledge helpful discussions with Drs. D. Y. Sogah and L. Wilczek.

References and Notes

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Registry No. IBVE (homopolymer), 9003-44-5; IBVE, 109-53-5; TfOH, 1493-13-6; EVE, 109-92-2; $EtAlCl_2$, 563-43-9; BF_3, 7637-07-2; CH_3SCH_3, 75-18-3; $S(Et)_2$, 352-93-2; S(Pr-*n*)$_2$, 111-47-7; S(*n*-Bu)$_2$, 544-40-1; S(*tert*-Bu)$_2$, 107-47-1; S(*sec*-Bu)$_2$, 626-26-6; S(*iso*-Bu)$_2$, 592-65-4; S(*iso*-Pr)$_2$, 625-80-9; MeSBu-*tert*, 6163-64-0; tetrahydrothiophene, 110-01-0.

Configurational and Conformational Characteristics of the Diastereoisomers of Bis(*o*-chlorophenyl) 2,4-Dimethylglutarate

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ABSTRACT: The meso and racemic isomers of bis(*o*-chlorophenyl) 2,4-dimethylglutarate were separated by fractional crystallization in hot heptane. The racemic isomer is crystalline with a melting point of 360 ± 1 K whereas the meso is liquid at room temperature. From the analysis of the ^{1}H and ^{13}C NMR spectra of both isomers it can be concluded that the former is predominantly in the tt conformation ($f_{tt} = 0.82$ and $f_{gg} = 0.18$), whereas the latter is in tg conformations. Dielectric measurements were performed at 30 °C in benzene solution, giving values of 5.70 D^2 and 6.07 D^2 for the mean-square dipole moment of the meso and racemic isomers, respectively. Critical analysis of the dipole moments was used to obtain information on the statistical weights, which account for the two possible rotational angles about the C_α–CO bonds, and the value of the rotational angle about the ortho phenyl bonds.

Introduction

High-resolution NMR spectroscopy has been a powerful tool in the determination of the stereochemical configuration of a great number of asymmetric polymers.[1] However, the fact that stereoregularity effects may be superimposed upon conformational effects, leading to an ambiguous resolution of the resonance peaks, makes advisable the analysis of the NMR spectra of model compounds in order to interpret the spectra of polymers in terms of their stereochemical configurations. In this regard, several derivatives of 2,4-dimethylpentane and 2,4,6-trisubstituted heptanes have been extensively studied from a microstructural point of view, as model compounds of vinyl and acrylic polymers.[2–5] However, the isolation of the meso and racemic components of the low molecular weight model compounds is a difficult task in many cases and, consequently, the NMR spectra of only a limited number of stereoisomers have been studied so far.[6–11]

Low molecular weight compounds have also been used to obtain information on the conformational energies and rotational angles of polymers with structural features similar to those of the model compounds.[12] Thus, the dipole moments of several phenyl and halophenyl derivatives of 2,4-dimethylglutaric acid have recently been measured,[13] and the results were interpreted by using statistical mechanics procedures as a first step to a further analysis of the conformation-dependent properties of poly(phenyl acrylate) and its halogenated derivatives. It was found that the dipole moments of chlorophenyl esters of 2,4-dimethylglutaric acid are strongly dependent on the location (ortho, metha, or para) of the chlorine atom in the phenyl ring. Thus, whereas the value of the mean-square dipole moment of bis(*o*-chlorophenyl) 2,4-dimethylglutarate (OCPDG) is 6.17 D^2 (close to the value of 4.40 D^2 found for diphenyl 2,4-dimethylglutarate), the value of this quantity for bis(*m*-chlorophenyl) and bis(*p*-chlorophenyl) 2,4-dimethylglutarates amounts to 9.73 and 10.30 D^2, respectively, at the same temperature.[13] It is obvious that knowledge of the dipole moments corresponding to the meso and racemic components would assist the critical interpretation of the polarity of the molecules and, in addition, would help in the analysis of the conformation-dependent properties of poly(phenyl acrylates) and their phenyl halogenated derivatives.

This paper reports the synthesis, isolation and characterization of the meso and racemic stereoisomers of OCPDG, which can be considered the dimer analogous of isotactic and syndiotactic poly(*o*-chlorophenyl acrylate)s, respectively. The dielectric results were then theoretically interpreted, using the rotational isomeric state model, with the aim of obtaining more information on the conformations of these diester compounds.

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