Reactivity and Polymerization of Isopropenyl *tert*-Butyl Ketone: A Twisted α,β-Unsaturated Enone

Hiroshi Ito,* Scott A. MacDonald, and C. Grant Willson

IBM Almaden Research Center, San Jose, California 95120-6099

John W. Moore, H. M. Gharapetian, and James E. Guillet

Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada.
Received November 6, 1985

ABSTRACT: Isopropenyl *tert*-butyl ketone (IPTBK) does not undergo radical homopolymerization under standard conditions. Anionic polymerization is an equilibrium process with a ceiling temperature below 0 °C and is quite sluggish. The low polymerizability of IPTBK in contrast to the high reactivity of typical vinyl ketones can be explained in terms of the high electron density on the β-carbon resulting from distortion of the usual planar s-cis or s-trans conformation. This monomer is not a fully conjugated system due to the bulky *tert*-butyl group. The presence of the unconjugative, twisted conformation has been confirmed by ^1H and ^{13}C NMR and UV spectroscopies. Nevertheless, high molecular weight polymers have been synthesized by anionic polymerization with *n*-butyllithium/18-crown-6 in tetrahydrofuran at −78 °C.

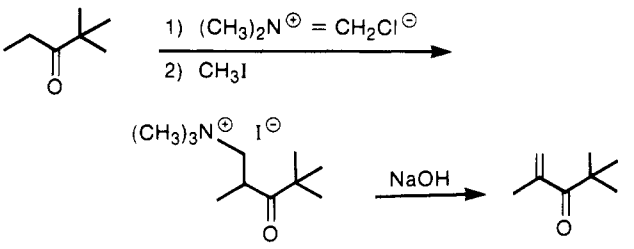
α,β-Unsaturated ketones are a class of vinyl monomers that have been very thoroughly studied with respect to their reactivity and polymerization mechanism and are considered to be among the most reactive vinyl monomers.[2,3] The photochemical degradation of vinyl ketone polymers[4] has been the subject of a number of fundamental studies. The photosensitivity of these materials has led to industrial applications.[5,6]

Poly(methyl isopropenyl ketone) (PMIPK) undergoes molecular weight reduction by main-chain scission upon exposure to electron-beam or UV radiation and has been used as a positive resist for semiconductor fabrication.[7] PMIPK is relatively insensitive to UV radiation compared to common photoresists, although the lithographic sensitivity can be improved by adding compounds such as 3,4-dimethoxybenzoic acid, which reportedly act as "sensitizers".[6]

Poly(vinyl ketones) undergo chain scission upon radiation by two pathways, Norrish type I and type II cleavages. In resist applications, the material is irradiated in the glassy state below the glass transition temperature (T_g). Under these conditions the Norrish type I pathway predominates as the cleavage mechanism, presumably because of the higher mobility required to achieve the cyclic transition state that the Norrish type II mechanism demands. The realization that the type I mechanism is the primary pathway responsible for lithographic application led us to study an analogue of PMIPK, poly(isopropenyl *tert*-butyl ketone) (PIPTBK), in which the structure has been modified for optimization of the type I cleavage reaction.

The initial step of the Norrish type I cleavage involves homolysis of a C–C bond adjacent to the carbonyl group. In PMIPK, this homolysis yields either an acyl radical and a tertiary radical or an acyl radical and a methyl radical. Cleavage to produce the tertiary backbone radical would seem to be greatly favored in terms of leading to net reaction simply on the basis of the much greater stability of this radical compared to the methyl radical generated by the alternative homolysis. A comparison of the quantum efficiencies for type I cleavage of acetone vs. di-*tert*-butyl ketone is one indication of this preference. PIPTBK undergoes type I homolysis to provide an acyl radical and a tertiary radical regardless of the cleavage site. We therefore reasoned that PIPTBK should have a significantly higher lithographic sensitivity than PMIPK. A determination of the scission quantum efficiency of these polymers will be reported in a future paper.[8]

Scheme I
Synthesis of 2,4,4-Trimethylpenten-3-one (I)



Experimental Section

Monomer Synthesis. The monomer, 2,4,4-trimethylpenten-3-one, has been reported in the literature.[9] However, the scheme used by these workers does not conveniently produce gram quantities of IPTBK. The synthetic procedure used in our study is outlined in Scheme I and has been successfully run on a 0.2-mol scale. This enone was obtained by allowing 2,2-dimethyl-3-pentanone to react with a 20% excess of *N,N*-dimethylmethyleneimmonium chloride in refluxing acetonitrile. The amine was alkylated with an excess of methyl iodide in methanol at room temperature to yield the quaternary ammonium salt. Elimination of trimethylamine in a 5% sodium hydroxide solution followed by distillation under reduced pressure (70 °C (80 mmHg)) afforded the desired monomer in 61% overall yield. Anal. Calcd for $C_8H_{14}O$: C, 76.19; H, 11.11. Found: C, 75.98; H, 10.90. ^1H NMR (90 MHz) δ 1.23 (s, 9 H, C_4H_9), 1.90 (t, 3 H, CH_3), 5.39 (m, 2 H, βCH_2). ^{13}C NMR (20 MHz) δ 20.55 (CH_3), 27.29 (C_4H_9), 117.48 (βCH_2), 208.7 (C=O).

Radical Homopolymerization Experiments. Radical homopolymerization of IPTBK was attempted under several conditions as detailed in Table I, but all such experiments failed to yield polymer. In a representative experiment, IPTBK (1.0 g) and azobis(isobutyronitrile) (AIBN, 0.5 mol % to the monomer) were placed in a dry polymerization ampule. The tube was degassed and sealed under vacuum. The mixture was allowed to stand at 70 °C for 3 days. No polymerization occurred as evidenced by recovery of monomer and failure to produce a methanol-insoluble fraction. Initiation by benzoyl peroxide (BPO, 5 mol %) did not produce a polymer.

Radical Copolymerization. Radical copolymerizations of IPTBK with methyl methacrylate (MMA) and styrene (St) were carried out in bulk with 5 and 0.1 mol % of BPO as an initiator at 70 °C for 3 days as well as homopolymerizations of each comonomer. The copolymers were first isolated by freeze-drying, weighed, purified by precipitation in methanol, and dried in a vacuum oven. The copolymer composition was determined by

0024-9297/86/2219-1839$01.50/0

Table I
Polymerization of IPTBK

polymn. no.	IPTBK feed	initiator (mol %)	solvent (mL)	temp, °C	time, h	yield, g	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$
	1.0 g	AIBN (0.5)		70	72	0		
	1.0 g	AIBN (0.5)	toluene (1.0)	75–80	72	0		
6[a]	0.5 mL	*n*-BuLi (1.6)	THF (0.5)	−78	24	0.006		
8	0.5 mL	PhMgBr (1.3)	toluene (0.5)	0	72	trace		
10	0.5 mL	*n*-BuLi/18-crown-6 (1.3)	toluene (0.5)	0	111	trace		
16	0.5 mL	*n*-BuLi/18-crown-6(1.3)	toluene (0.5)	−78	192	0.025	34.7[b]	133[b]
31	0.5 mL	*n*-BuLi/18-crown-6 (5.1)	THF (0.5)	−78	72	0.211	17.3[b]	24.6[b]
45	6.0 mL	*n*-BuLi/18-crown-6 (5.1)	THF (6.0)	−78	72	3.961	7.9[c]	18.0[d]
88	2.5 mL	*n*-BuLi/18-crown-6 (5.0)	THF (2.5)	−78	96	1.281	23.7[e]	48.0[d]
91	10.0 mL	*n*-BuLi/18-crown-6 (5.0)	THF (10.0)	−78	72	5.918	9.9[e]	

[a] Methanol-soluble fraction 17 mg. [b] GPC (THF), relative to polystyrene. [c] Vapor pressure osmometry. [d] Low-angle laser light scattering. [e] Membrane osmometry.

elemental analysis and ^1H NMR.

Anionic Homopolymerization. Anionic polymerizations were carried out under high vacuum with use of a break-seal technique. Preparation of initiators, purification of monomers and solvents, and polymerization procedures have been previously described.[10] Detailed polymerization conditions are shown in Table I. Polymerization was terminated by adding cold methanol to the polymerization mixture at the polymerization temperature. The resulting mixture was dissolved in chloroform and then poured into a large excess of stirred methanol. The polymer was reprecipitated in methanol, isolated by filtration, and dried in vacuo at about 40 °C. Anal. Calcd for $C_8H_{14}O$ (no. 91): C, 76.19; H, 11.11. Found: C, 76.22; H, 11.28.

Attempted Cationic and Anionic Copolymerizations. Cationic polymerizations of IPTBK and α-methylstyrene (αMeSt) attempted with boron trifluoride etherate (BF_3OEt_2) as an initiator in dichloromethane or in liquid sulfur dioxide resulted in the formation of a homopolymer of αMeSt. The purification of sulfur dioxide and polymerization in this solvent have been previously described.[11] Anionic copolymerization of IPTBK and αMeSt by *n*-butyllithium (*n*-BuLi) in the presence of 18-crown-6 at −78 °C produced a small amount of PIPTBK. The conditions and results of the copolymerizations are summarized in Table VI.

Measurements. NMR spectra were recorded in deuteriochloroform ($CDCl_3$) unless otherwise indicated on Varian EM-390 (^1H), IBM NR-80 (^1H), and Varian CFT-20 (^1H and ^{13}C) spectrometers. IR spectra were recorded on a Perkin-Elmer 283 spectrometer. Molecular weight determinations were made with a Wescan 230 recording membrane osmometer or Hewlett-Packard 502 high-speed membrane osmometer with toluene or dioxane, respectively, as a solvent while GPC measurements were performed on a Waters Model 150 chromatograph equipped with six μStyragel columns at 30 °C in tetrahydrofuran (THF). A Hewlett-Packard 302B vapor phase osmometer was also used for molecular weight determination in toluene. Weight-average molecular weights were measured on a Chromatix KMX6 low-angle laser light scattering instrument, and the refactive index was determined with a Brice Phoenix BP2000V differential refractometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on a Du Pont 1090 instrument at a heating rate of 5 °C/min.

Results and Discussion

Radical Polymerization. The homopolymerization of 2,2,4-trimethylpenten-3-one (IPTBK) by radical initiation has been reported in the patent literature.[12] However, as detailed below, we have found this monomer to have unique properties that render the claim of radical polymerization suspect.

Since, as stated in the introduction, vinyl ketones as a class are very reactive toward radical polymerization and because of the earlier claim of a successful radical polymerization of IPTBK, we assumed that preparation of the polymer would be straightforward. However, as shown in Table I, our attempts to repeat the published preparation all failed. Neither AIBN nor BPO produced a polymer, even at high initiator concentrations in bulk or in solution under standard polymerization conditions. Consequently, we studied radical copolymerization of IPTBK with St and MMA.

Table II
Radical Copolymerization of IPTBK with St and MMA[a]

monomer	yield, %	M_n	% ketone ^1H	% ketone C, H
IPTBK	0			
IPTBK/St (1/1)	25	34 700	41	39
IPTBK/MMA (1/1)	17	27 500	31	28
St	92	121 000		
MMA	95	1 030 000		

[a] Bulk, 0.1% BPO, 70 °C, 3 days.

The results of the copolymerization studies are summarized in Table II. Copolymerization of IPTBK with St and MMA initiated with 0.1 mol % of BPO at 70 °C at monomer mole ratios of 1:1 showed that introduction of IPTBK dramatically reduces both the yield of polymer and the molecular weight of the product. In the copolymerization of St, the yield was only 25%, whereas the homopolymerization of St under the same conditions provided 92% yield. The number-average molecular weight of the copolymer was 34 700, whereas the corresponding St homopolymer had M_n = 121 000. Similar results were obtained with MMA. The yield dropped from 95% for the homopolymer to 17% for the copolymer, and the molecular weight was reduced from 1 030 000 to 27 500. The 1:1 copolymerization of IPTBK with St and MMA resulted in incorporation of about 40 and 30% of IPTBK, respectively, in the copolymers.

The low incorporation of IPTBK in the copolymers indicates that IPTBK is less reactive than either St or MMA, whereas the dramatic yield reduction and lower molecular weight of the copolymers is indicative of a chain transfer and/or termination unique to IPTBK. Degradative chain transfer to the α-methyl group of IPTBK is one reasonable explanation for these observations.

Anionic Polymerization. Since vinyl ketones are known to be very reactive in anionic polymerization, we carried out several anionic polymerizations as shown in Table I. *n*-BuLi, one of the most reactive anionic initiators that can initiate the polymerization of the least reactive, nonpolar vinyl monomers, produced only a trace of polymer in THF at −78 °C (polymerization no. 6). Initiation by phenylmagnesium bromide (PhMgBr) in toluene at 0 °C was not very successful (no. 8). The addition of 18-crown-6 to *n*-BuLi did not help when the polymerization was carried out in toluene at 0 °C (no. 10). However, we were very much encouraged by obtaining a high molecular weight polymer (M_n = 34 700 and M_w = 133 000 by GPC) in a polymerization with *n*-BuLi/18-crown-6 in toluene at −78 °C, though the yield was still low (no. 16). The re-

placement of toluene with THF and the use of a high concentration (5%) of *n*-BuLi/18-crown-6 constantly produced a high polymer in about 50% yield when the reaction was carried out at −78 °C. All the reagents were mixed at room temperature and then cooled to −78 °C. At the early stage, some precipitates were formed and then the polymerization mixture solidified upon standing at −78 °C. In one instance (no. 88), the polymerization mixture was accidentally warmed to −5 °C over the weekend, resulting in a loss of the high viscosity gained by the successful polymerization at −78 °C. Termination at this stage failed to afford a polymer. However, cooling of the system again to −78 °C restored the viscosity to the stage where the mixture was completely solidified. This observation indicates that the polymerization of IPTBK is an equilibrium reaction and the ceiling temperature (T_c) lies well below 0 °C. Thus, our earlier unsuccessful attempts at 0 °C (no. 8 and 10) may be well explained in terms of the low T_c. However, since *n*-BuLi in THF at −78 °C failed to initiate polymerization (no. 6), PhMgBr, a weaker initiator, may not be effective even at −78 °C. The resistance to radical homopolymerization could also be interpreted in terms of the equilibrium and the low T_c. In order to clarify this point, low-temperature radical polymerizations by γ-irradiation or by use of low-temperature initiators are planned. In any event, IPTBK appears to be one of the most unreactive vinyl monomers, while methyl vinyl ketone is reactive enough to be polymerized by initiators such as trialkylaluminum or dialkylzinc that fail to polymerize MMA or acryronitrile. Overberger and Schiller have reported that anionic copolymerization of *tert*-butyl vinyl ketone (TBVK) with MMA yields only a homopolymer of TBVK, indicating a higher reactivity of TBVK than MMA,[13] and Hatada and his co-workers have recently shown that *n*-butyl isopropenyl ketone reacts faster than MMA with growing anions.[14] Thus, the dramatic reduction in the reactivity in IPTBK is quite evident.

18-Crown-6 apparently enhances the reactivity of *n*-BuLi in the anionic polymerization of IPTBK. The increased initiator reactivity by a formation of "coordination-agent-separated ion pairs" is well-known. For example, Tsuruta and his co-workers have reported the effect of the addition of poly(ethylene oxide), or poly(propylene oxide),[15] or alkoxyethanol[16] on the reactivity of *n*-BuLi. They have also promoted the reactivity of magnesium alkyl to such an extent by adding 2-alkoxyethanol that the complex initiator can polymerize St, which does not form a polymer by initiation with an alkylmagnesium compound alone.[17] Smid and his colleagues have observed agent-separated ion pairs in systems of organolithium compounds with crown ethers.[18,19] Though the cavity of 18-crown-6 (4 Å) may not be optimum for Li^+ ions (1.20 Å), we used this particular crown ether because of its easier purification compared with liquid 12-crown-4.

Spectroscopic Studies. In order to understand why IPTBK does not undergo radical homopolymerization under conditions that produce high polymer from analogous vinyl ketone monomers, a detailed study of this interesting monomer was undertaken. The results of these analyses confirm the suggestion derived from examining space-filling models of IPTBK; i.e., this monomer appears to prefer a nonconjugated, twisted conformation due to the large steric demand of the *tert*-butyl group. French scientists have studied the conformation of nine α,β-unsaturated ketones including IPTBK by ^1H NMR, IR, and UV spectroscopies and documented the existence of an equilibrium between the s-trans form and the twisted conformation (Scheme II).[20] The most outstanding feature

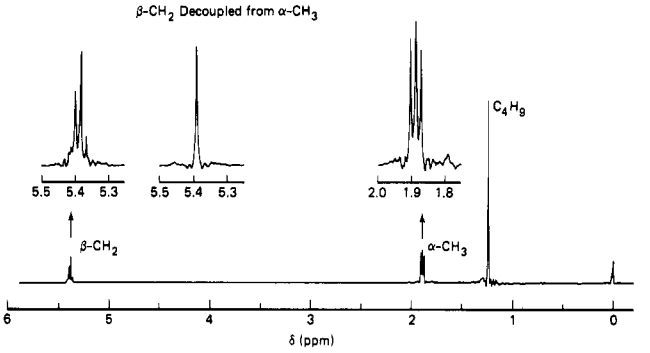
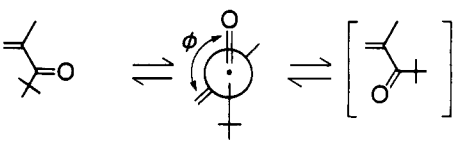
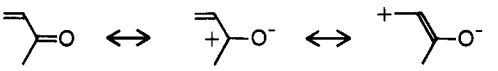


Figure 1. 80-MHz ^1H NMR spectrum of IPTBK in $CDCl_3$.

Scheme II
Conformation of IPTBK



Scheme III
Conjugation in Vinyl Ketones



of the ^1H NMR spectrum of IPTBK (Figure 1) is a singlet βCH_2 resonance (5.39 ppm) decoupled from the α-methyl resonance, indicating that the methylene protons are more or less magnetically equivalent. It has been reported that the difference between the βCH_2 chemical shifts ranges from ca. 0.7 (s-cis) to ca. 0.15 ppm (s-trans) in alkyl vinyl ketones.[21] The chemical shift difference significantly smaller than 0.15 ppm suggests that the contribution of the nonplanar, twisted conformation is large in the equilibrium. While conjugative vinyl monomers show a fairly large chemical shift difference between the β protons (ca. 0.2 ppm with MIPK and ca. 0.5 ppm with MMA), unconjugative vinyl monomers such as isopropenyl acetate and isopropenyl halides exhibit a smaller chemical shift difference.[22] Although the AB degeneracies can be in general removed by employing benzene as a solvent, the β-methylene resonance of IPTBK showed only a small separation amounting to 0.06 ppm even in this solvent. Another interesting feature of the ^1H NMR spectrum of IPTBK is the high chemical shift of the β-protons (5.39 ppm), which is very close to those of αMeSt (5.04 and 5.28 ppm), isopropenyl chloride (5.08 ppm), and isopropenyl bromide (5.53 ppm), while the corresponding resonance in typical conjugated acrylates and vinyl ketones occurs at about 6 ppm.

^{13}C NMR further provides added evidence for the reduced conjugation between the carbonyl and vinyl π system in IPTBK. In conjugative, α,β-unsaturated ketone systems, the positive charge on the carbonyl carbon resulting from polarization is compensated by electron flow from the C=C bond, resulting in reduced electron density on the β-carbon (Scheme III). Consequently, the β-carbon resonance in conjugative vinyl ketone systems occurs at lower field than that of the corresponding alkenes, and the carbonyl carbon resonates at a higher field than that of the corresponding saturated ketones. In contrast, if the system is not conjugated due to steric hindrance, delocalization does not take place, resulting in ^{13}C resonances similar to the saturated ketones or alkenes. The high chemical shift of the β protons of IPTBK was mentioned earlier. Since ^{13}C NMR has proven to be an excellent

Table III
β-Carbon Chemical Shift[a] of Enones and Alkenes

substitution	enone (a)	alkene (b)	Δ
I	117.7	114.2	3.5
II	127.6	116.7	10.9
III	125.3	109.1	16.2
IV	128.7	113.3	15.4

[a] Chemical shift ppm downfield from Me_4Si.

Table IV
Carbonyl Chemical Shift[a] of Enones and Ketones

substitution	enone (a)	ketone (c)	Δ
I	208.7	217.1	8.4
II	202.4	213.8	11.4
III	199.1	210.4	11.3
IV	198.3	207.6	9.3

[a] Chemical shift ppm downfield from Me_4Si.

Table V
UV Absorption of Enones in MeOH

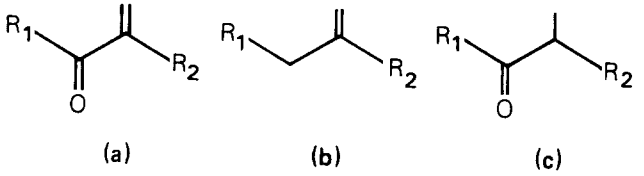
enone	λ_{max}, nm	ϵ_{max}
Ia	220	4100
IIIa	218	8000
IVa	213	7100

means of studying monomer conformation and electron densities, we have prepared or purchased several related vinyl ketones, corresponding alkenes, and saturated ketones and measured ^{13}C chemical shifts in neat (Chart I). In Table III are summarized β-carbon chemical shifts of the enones and corresponding alkenes. The β-carbon of IPTBK resonates at a very high field (117.7 ppm), much closer to that of the corresponding alkenes (109–117 ppm) than any of the other vinyl ketones studied (125–129 ppm). The β-carbon chemical shift difference (Δ) between the enone and the corresponding alkene is much smaller in the case of IPTBK (3.5 ppm) than in the other systems (11–16 ppm).

The chemical shifts of the carbonyl carbon of the enones and their corresponding saturated analogues are provided in Table IV. The carbonyl carbon of IPTBK resonates at a lower field (208.7 ppm), in the same range as the saturated ketones (208–217 ppm), than the other enones and stands clearly apart from the conjugative enones which have carbonyl carbon resonances between 198 and 202 ppm. The carbonyl chemical shift difference between the enone and its saturated analogue is again smaller for IPTBK, but the difference is not nearly as significant as in the comparison of the β-carbon resonance of the enone with its alkene analogue. Our ^{13}C NMR studies clearly indicate that IPTBK is not a fully conjugated system, presumably due to steric hindrance.

UV spectroscopy also provides information about the preferred conformation of vinyl ketones as shown in Table V. The $\pi \rightarrow \pi^*$ transition suffers a bathochromic shift and a reduction in extinction coefficient as steric hindrance increases.[20] The conformation of these compounds has also been studied by IR. These studies have shown that IPTBK and other isopropenyl ketones exist in an equilibrium between the s-trans and the twisted conformation in which

Chart I
Enones, Alkenes, and Ketones



I: R_1 = tBu, R_2 = Me

II: R_1 = tBu, R_2 = H

III: R_1 = Me, R_2 = Me

IV: R_1 = Me, R_2 = H

the dihedral angle (Φ) between the two π systems is about 120° (Scheme II).[20]

Naito et al.[21] have spectroscopically studied the conformation of several alkyl vinyl ketones excluding IPTBK. According to their studies MIPK prefers the s-trans form almost exclusively (98%), while the equilibrium of TBVK shifts predominantly toward the s-cis conformer (92%). IPTBK has the characteristics of both of these compounds and appears to prefer neither extreme but, rather, a twisted form that prevents electron delocalization.

If IPTBK exists in the twisted form, two enantiomers are expected to be detected by NMR with use of chiral shift reagent. The ^1H NMR chemical shift of IPTBK complexed with varying amounts of tris[3-((trifluoromethyl)hydroxymethylene)-*d*-camphorato]europium(III), $Eu(tfc)_3$, was measured in carbon tetrachloride (CCl_4) at 90 MHz. All the signals linearly shifted to lower field with increasing shift reagent concentration, as expected. The β-proton resonances exhibited a good separation upon addition of the reagent to such an extent that the chemical shift difference was 0.36 ppm at 15% of $Eu(tfc)_3$. However, none of the signals exhibited a separation due to the two enantiomers. The successful separation of two enantiomers may require a low-temperature NMR study.

Attempted Ionic Copolymerizations with αMeSt. As mentioned earlier, the β-carbon and protons of IPTBK resonate at much higher field than one can expect from the related vinyl monomers. Since the chemical shifts are fairly close to those of αMeSt and because of the high electron density on the β-carbon, we attempted cationic copolymerization of IPTBK with αMeSt as shown in Table VI. Initiation with BF_3OEt_2 in dichloromethane yielded only the homopolymer of αMeSt. Using liquid sulfur dioxide as a solvent did not change the course of the reaction, though the yield of poly(α-methylstyrene) was increased. Ito et al.[11] have previously observed that carbonyl functionality appears to be protected from attack by the cationic initiator or by the growing cation in this unique solvent. Methyl acrylate is known to undergo cationic copolymerization with St in liquid sulfur dioxide.[23] Anionic copolymerization of IPTBK with αMeSt produced a homopolymer of IPTBK as shown in Table VI.

Table VI
Attempted Copolymerization of IPTBK with α-Methylstyrene (αMeSt)

polymn. no.	IPTBK feed, mL	αMeSt feed, mL	initiator (mol %)	solvent (mL)	temp, °C	time, h	yield, g	product
19	0.5	0.5	BF_3OEt_2 (1.9)	CH_2Cl_2 (1.0)	−78	288	0.011	PαMeSt
21	0.5	0.5	BF_3OEt_2 (1.0)	liq SO_2 (1.0)	−60	48	0.416	PαMeSt
26	0.5	0.5	*n*-BuLi/18-crown-6 (1.2)	toluene (1.0)	−78	120	0.005	PIPTBK

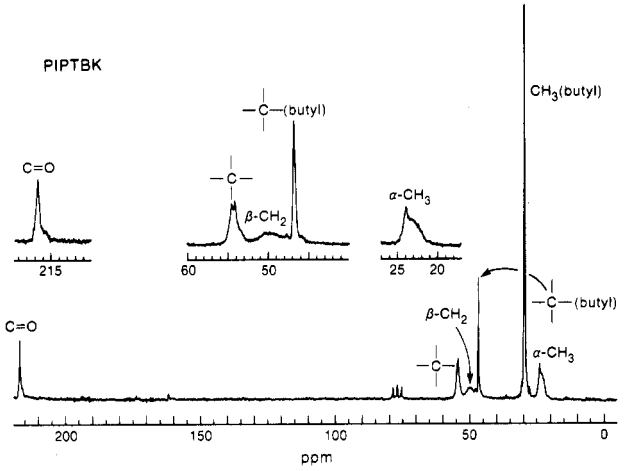


Figure 2. 20-MHz ^{13}C NMR spectrum of PIPTBK in $CDCl_3$.

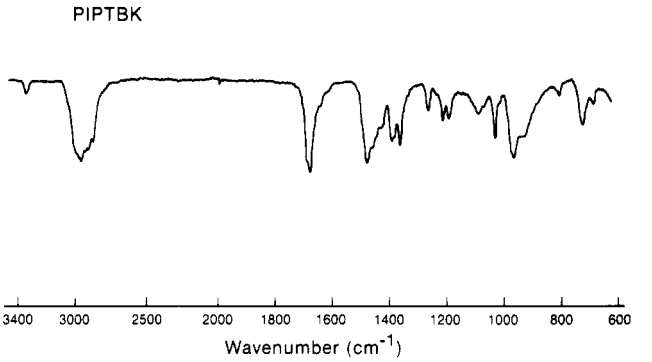


Figure 3. IR spectrum of PIPTBK film.

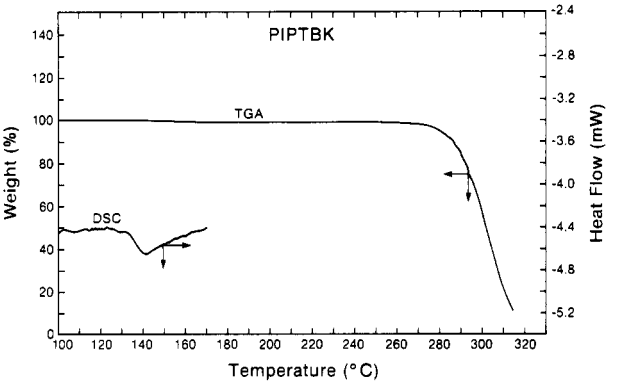


Figure 4. TGA and DSC of PIPTBK (heating rate: 5 °C/min).

Summary. Because of the bulky *tert*-butyl group, IPTBK prefers the twisted conformation, which does not allow delocalization of the π electrons, thus leaving a high electron density on the β-carbon, as evidenced by our spectroscopic studies. The poor conjugation (low Q) and the high electron density (low e) are responsible for the low reactivity of IPTBK in radical and anionic polymerizations. Unconjugative vinyl monomers are known to be less reactive toward radical and carbanions. If one applies the linear relationship between ^{13}C chemical shift and e value of vinyl monomers derived by Herman and Teyssie[24] to IPTBK (because of the large steric factor in this system, the applicability may be questionable), the e value of IPTBK can be estimated to be about 0.2, very close to that of vinyl chloride. Kawabata, Tsuruta, and Furukawa have proposed a revised Q–e scheme and found two separate linear relationships between Q and e for conjugative and unconjugative vinyl monomers.[25] According to the revised Q–e map, the resonance stabilization factor (Q) of IPTBK is very similar to that of vinyl chloride, if the steric factor can be neglected in this scheme. The reduction in the yield and molecular weight observed in the radical copolymerizations of IPTBK with MMA and St could be due to the degradative chain transfer to the α-methyl group of IPTBK. This type of chain transfer is well-known in radical polymerization of unconjugative isopropenyl or allyl monomers, which upon H radical abstraction form a resonance-stabilized allyl radical that is incapable of reinitiating the polymerization. Conjugative vinyl monomers are more reactive toward radicals or carbanions, while radicals and anions derived from conjugative monomers are less reactive due to resonance stabilization. In contrast, unconjugative monomers are less reactive, but their radicals and carbanions are more reactive. IPTBK suffers the worst of both worlds. The monomer is not very reactive toward radicals and anions due to poor conjugation, but once addition has occurred, there is sufficient delocalization to render the growing chain end as unreactive as its conjugated counterparts.

NMR, IR, and Thermal Analysis of PIPTBK. The ^{13}C NMR (Figure 2) and IR (Figure 3) spectra of PIPTBK synthesized by *n*-BuLi/18-crown-6 initiation in THF at −78 °C indicate that the polymer thus obtained is a vinyl-addition product without detectable participation of the carbonyl functionality. The α-methyl, carbonyl, and α-carbon signals are indicative of tacticity. PIPTBK is thermally stable to 280 °C and then sharply decomposes as indicated by TGA in Figure 4. According to the DSC curve shown in Figure 4, the glass transition temperature of PIPTBK is about 135 °C, which should be contrasted with 20 °C for PMIPK.

Conclusions

1. IPTBK prefers a twisted conformation due to the large steric demand of the *tert*-butyl group and therefore is not fully conjugated.
2. Because of the poor conjugation, IPTBK is reluctant to undergo radical homopolymerization, and successful anionic polymerization requires a very nucleophilic initiator.
3. Anionic polymerization appears to be an equilibrium reaction with a ceiling temperature below 0 °C.
4. Although the β-carbon of IPTBK has high electron density, this monomer is extremely unreactive in cationic copolymerization with αMeSt.

Acknowledgment. We are grateful to W. Fleming, C. Hrusa, C. Cole, and R. Siemens for their technical assistance in NMR, GPC, and thermal analysis.

Registry No. IPTBK, 7432-56-6; (IPTBK)·(MMA) (copolymer), 102233-59-0; (IPTBK)·(St) (copolymer), 102233-60-3; IPTBK (homopolymer), 90337-66-9; $H_3CCH_2COC(CH_3)_3$, 564-04-5; $(CH_3)_2N^+{=}CH_2Cl^-$, 30354-18-8.

References and Notes

(1) This work was presented in part at the ACS National Meeting, St. Louis, MO, April 1984, and at the 1st SPSJ International Polymer Conference, Kyoto, Japan, August 1984.
(2) Coleman, L. E., Jr.; Meinhardt, N. A. *Fortschr. Hochpolym.-Forsch.* **1959**, *1*, 159.
(3) Lyons, A. R. *J. Polym. Sci., Part D* **1972**, 251.
(4) Dan, E.; Somersall, A. C.; Guillet, J. E. *Macromolecules* **1973**, *6*, 228 and references therein.
(5) Levine, A. W.; Kaplan, M.; Poliniak, E. S. *Polym. Eng. Sci.* **1974**, *14*, 518.
(6) Tsuda, M.; Oikawa, S.; Nakamura, Y.; Nagata, H.; Yokota, A.; Nakane, H.; Tsumori, T.; Nakane, Y.; Mifune, T. *Photogr. Sci. Eng.* **1979**, *23*, 290.
(7) Watts, M. P. C. *Proc. SPIE Int. Soc. Opt Eng.* **1984**, *469*, 2.

(8) Moore, J. W.; Gharapetian, H. M.; Guillet, J. E.; Ito, H.; MacDonald, S. A.; Willson, C. G., in preparation.
(9) Crandall, J. K.; Chang, L.-H. *J. Org. Chem.* **1967**, *32*, 435.
(10) Ito, H.; Miller, D. C.; Willson, C. G. *Macromolecules* **1982**, *15*, 915.
(11) Ito, H.; Willson, C. G.; Frechet, J. M. J.; Farrall, J. M.; Eichler, E. *Macromolecules* **1983**, *16*, 510.
(12) Michaelsen, J. D. U. S. Patent 3 091 532, 1963.
(13) Overberger, C. G.; Schiller, A. M. *J. Polym. Sci., Part C* **1963**, *1*, 325.
(14) Hatada, K.; Kitayama, T.; Okahata, S.; Yuki, H. *Prepr. 43rd Spring Meeting Chem. Soc. Jpn.* **1981**, 1118.
(15) Narita, T.; Imai, N.; Tsuruta, T. *Kogyo Kagaku Zasshi* **1969**, *72*, 994.
(16) Narita, T.; Masaki, A.; Tsuruta, T. *J. Macromol. Sci., Chem.* **1970**, *A4*, 277.
(17) Narita, T.; Yasumura, T.; Tsuruta, T. *Polym. J. (Tokyo)* **1973**, *4*, 421.
(18) Wong, K. H.; Konizer, G.; Smid, J. *J. Am. Chem. Soc.* **1970**, *92*, 666.
(19) Takaki, U.; Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1971**, *93*, 6760.
(20) Bienvenue, A.; Duchatellier, B. *Tetrahedron* **1972**, *28*, 833.
(21) Naito, I.; Kinoshita, A.; Yonemitsu, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 339.
(22) Jackman, L. M.; Wiley, R. H. *J. Chem. Soc.* **1960**, 2881.
(23) Matsuda, M.; Ohshima, K.; Tokura, N. *J. Polym. Sci., Part A* **1964**, *2*, 4271.
(24) Herman, J. J.; Teyssie, Ph. *Macromolecules* **1978**, *11*, 839.
(25) Kawabata, N.; Tsuruta, T.; Furukawa, J. *Makromol. Chem.* **1962**, *51*, 70.
(26) **Note Added in Proof**: After this paper had been submitted for publication, we found an article (Kinoshita, A.; Naito, I. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 359) describing radical copolymerizations of alkyl isopropenyl ketones including IPT-BK with styrene.

Molecular Structure and Electronic Property Modification of Poly(diacetylenes)

B. J. Orchard and S. K. Tripathy*

GTE Laboratories Incorporated, Waltham, Massachusetts 02254.
Received December 10, 1985

ABSTRACT: The electronic properties of poly(diacetylenes) were investigated by using the valence effective Hamiltonian (VEH) method. The molecular geometries considered were appropriately optimized. The relative effects of the polymer backbone geometry, the presence of conformational defects along the polymer chain backbone, the chemical/electronic nature of the substituents, and the conformation of the side groups upon the electronic structure were investigated.

I. Introduction

The electronic and optical properties of poly(diacetylenes) have received considerable attention.[1,2] This interest stems from two important considerations: First, poly(diacetylenes) belong to a unique class of macromolecules that can be crystallized to form macroscopic defect-free single crystals[3] with the extended-chain unsaturated backbones stacked parallel to each other. The crystals display a number of different morphologies. The many different side groups that can be part of the monomer structure have a strong influence on the crystalline organization and polymerization behavior in the solid state. Second, the one-dimensional nature of the unsaturated poly(diacetylene) structure implies novel electronic and optical properties. Large and fast (approximately ps) nonlinear optical coefficients have been predicted for these materials. Recent measurements have indeed confirmed these predictions.[4] The materials have the characteristic visible spectrum of a low dimensional semiconductor with an absorption edge in the mid-visible range.

Many fundamental details of these two unique aspects of the poly(diacetylenes) regarding the structural order and the one-dimensional electronic properties have been investigated in detail. Interestingly, however, most investigations dealing with the electronic and optical properties of the diacetylenes treat the lattice of side groups as an appendage whose only primary function is to hold the polymer chain backbones together at a fairly large distance from each other. Thus, most often the diacetylene system, for the electronic property aspects, is modeled as possessing an extended planar trans structure with hydrogen atoms serving as the side groups to satisfy the backbone valence geometry. Hence, most studies to date essentially decouple the electronic states of the side group from those of the backbone. This is not totally inconsistent with the experimental approaches that have been adopted. There are few examples of poly(diacetylene) where side groups have been designed to electronically couple with the backbone states. In one case, Wegner et al.[5] investigated a poly(diacetylene) system with a phenyl group adjacent to the polymer backbone, which would be expected to be more strongly coupled with the backbone, but poor monomer-to-polymer conversion was probably responsible for the lack of subsequent measurements of the electronic and optical properties.

It is clearly seen, however, that side-group organization does strongly influence the electronic properties of the backbone.[6] For example, the thermochromic properties of the poly(diacetylenes) are attributed to the side-group reorganization leading to a change in strain on the backbone. It is in this light that the present investigation was carried out to model the influence on the electronic structure of the backbone of two critical factors; the electronic structure of the side groups and their molecular arrangements vis-a-vis the backbone.

The approach adopted was to use established methodologies that have yielded a reasonable description of the isolated polymer backbone electronic structure in conjuction with molecular mechanics and full geometry optimization to extract the details of the structure property relationships.

In this paper, we report detailed investigations concerning the influence of molecular structure and conformation of the side groups upon the electron-density distribution of the backbone and the resulting electronic properties of the poly(diacetylene) system. Both proposed acetylenic and butatrienic structures were investigated so that the correlation between the chemical/electronic na-

0024-9297/86/2219-1844$01.50/0