Stereoregulation in the Free-Ion Propagation of Optically Active Alkyl Vinyl Ethers

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ABSTRACT: Trimethylvinyloxysilane (TMVO), (−)-menthyl vinyl ether (MVE), and (*S*)-1-methylpropyl vinyl ether (BVE) have been polymerized using tropylium hexachloroantimonate as cationic initiator under conditions in which free carbocations are the important propagating intermediates. The bulky and nonoptically active TMVO yielded highly syndiotactic polymers in accordance with current theories regarding stereoregulation in propagation by unassociated species such as free radicals. In complete contrast, the equally bulky but optically active MVE yielded highly isotactic polymers indicative of a pronounced chirality induced stereoregulation during the chain growth process. BVE yielded polymers having optical activity consistent with a degree of isotacticity approximately one half of that for the most isotactic fraction reported in the literature. Implications of these results for the mechanisms of cationic polymerization of alkyl vinyl ethers are discussed.

Stereoregularity of polymer chains formed from a simple vinyl monomer under conditions where the propagating species is thought to be free from hindrance by solvent, counterion, etc., is controlled by the difference in activation energies for the insertion of a monomer unit yielding an isotactic or syndiotactic diad, respectively.[1] Radical polymerizations are the best known of those involving "free" propagating species and it is now well established that in free-radical propagation, syndiotactic placements are slightly favored over isotactic placements with the difference becoming progressively more important as the polymerization temperature is lowered.[1]

In contrast to free-radical systems, propagation by ionic species is complicated by effects of medium and temperature on ion-pair dissociation equilibria and the inevitable stereochemical control resulting from association of counterion with the growing chain end.[1,2]

Studies of the polymerization of optically active monomers have been useful in helping to understand details of the stereospecific polymerization of several types of vinyl monomers.[3,4] Alkyl vinyl ethers constitute one such class of vinyl monomers known to give rise to both stereoregular and atactic polymers depending on catalyst types and reaction conditions.[5] In previous publications it has been shown that isotactic polymers from several optically active alkyl vinyl ethers are readily produced by polymerization with catalysts such as $EtAlCl_2$ in hydrocarbon solvents at low temperatures[6,7] and also, at ambient temperature, by heterogeneous catalysts derived from aluminum alkyls (or alkoxides) and sulfuric acid[8,9] and by aluminum sulfate based catalysts.[10,11]

In a general sense, both optically active 1-methylpropyl vinyl ether and (−)-menthyl vinyl ether have been useful in helping to correlate main-chain regularity with polymerization mechanism on account of the substantial enhancement of optical rotation (compared with low molecular weight model compounds) exhibited by the polymers shown to be highly isotactic by independent spectroscopic techniques (X-ray and IR).[12-14] This enhancement of optical rotation for isotactic poly(α-olefins) and poly(alkyl vinyl ethers) is explained as being due to the existence of a helical conformation of the main chain with a prevailing screw sense.[15,16]

Examination of all the published data suggests generally that formation of isotactic polymers from alkyl vinyl ethers requires the use of either incompletely characterized initiation and propagation systems or the presence of some separated phase (solid or liquid). Polymerization of alkyl vinyl ethers may be readily affected by reaction with stable carbocationic salts such as triphenyl methyl tetrafluoroborate and tropylium hexachloroantimonate[17,18] and this procedure has been adopted by Aso and Kunitake[19] in attempts to correlate stereoregularity of the alkyl vinyl ether polymer backbone with effects of the counterions used in the polymerizations.

Independently we have shown that such stable carbocation salts are effectively separated from their counterions in CH_2Cl_2 at concentrations less than 10^{-4}–10^{-5} M and that under such conditions polymerization of alkyl vinyl ethers occurs by propagation of free cations.[20] This technique affords the possibility to investigate homogeneous cationic polymerization of optically active vinyl ethers with propagation by freely dissociated cationic species. The optical activity of polymers produced under these conditions facilitates qualitative conclusions as to the stereoregulating influence of a chiral center, with a prevailing configuration, present in the monomer, on such freely propagating species.

Experimental Section

Materials. Dichloromethane and tropylium hexachloroantimonate ($C_7H_7SbCl_6$) were purified as previously described.[18] (1*R*,3*R*,4*S*)-1-Methyl-4-isopropylcyclohex-3-yl vinyl ether [(−)-menthyl vinyl ether] (MVE) {$[\alpha]^{25}_D$ −73.6 (neat)} (optical purity 100%)[21] and (*S*)-1-methylpropyl vinyl ether (BVE) {$[\alpha]^{25}_D$ + 13.0 (neat)} (optical purity 90.8%)[22] were prepared by transvinylation according to Watanabe and Conlon[23] with 55 and 56% yields, respectively. Trimethylvinyloxysilane (TVOS) was prepared by fractional distillation of the mixture obtained by refluxing an equimolar solution of trimethylchlorosilane, acetaldehyde, and triethylamine in pentane[24] (yield 15%).

All monomers were purified by distillation over Na/K alloy immediately before use.

Polymerization Experiments. The required amount of initiator (5×10^{-3} M solution of $C_7H_7SbCl_6$ in CH_2Cl_2) was rapidly injected by syringe through a rubber septum-capped vessel containing a stirred solution of the monomer. Temperatures of both catalyst and monomer solutions were adjusted to the appropriate value prior to the rapid mixing. Reaction mixtures were homogeneous throughout and were terminated, after approximately 20 min of reaction, by injection of 5 mL of methanol and then pouring the mixture into a large excess of methanol. The

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Table I
Polymerization of (−)-Menthyl Vinyl Ether (MVE) by Tropylium Hexachloroantimonate ($C_7H_7SbCl_6$) in Dichloromethane

run	[MVE], M	10^5-[$C_7H_7SbCl_6$], M	temp, °C	conv,[a] %	$[\alpha]^{25}_D$ [b]	$10^{-3}\overline{M}_n$ [c]	$\overline{DP}_n$
M1	1.1	110	0	93.1	−206	22	121
M2	1.1	11	0	72.5	−199	23	129
M3	0.18	1.8	0	63.1	−206	15	85
M4	0.18	1.8	−30	40.1	−209	12	66
M5	0.18	1.8	30	30.0	−202	5.5[d]	30

[a] Evaluated as (weight of polymer/weight of starting monomer) × 100. [b] In toluene solution (c = 1-3 g/dL). [c] In toluene at 37 °C by a membrane osmometer. [d] In benzene at 37 °C by vapor pressure osmometry.

Table II
Polymerization of (S)-1-Methylpropyl Vinyl Ether (BVE) by Tropylium Hexachloroantimonate ($C_7H_7SbCl_6$) in Dichloromethane

run	[BVE], M	10^5-[$C_7H_7SbCl_6$], M	temp, °C	conv,[a] %	$[\alpha]^{25}_D$ [b]	$10^{-3}\overline{M}_n$ [c]	$\overline{DP}_n$
B1	1.0	100	0	82.0	+146	7.2	72
B2	1.0	10	0	94.5	+147	7.7	77
B3	0.2	1	0	92.6	+143	5.8	58
B4	0.2	1	−30	83.1	+158	6.1	61
B5	0.2	1	30	80.2	+124	5.2	52

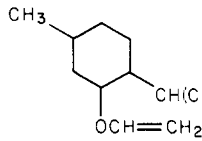
[a] Evaluated as (weight of polymer/weight of starting monomer) × 100. [b] In benzene solution (c = 1-3 g/dL). [c] In benzene at 37 °C by vapor pressure osmometry.

polymers were recovered as white, tacky to hard solids identical in appearance to those obtained by other polymerization catalysts.[6-11,18] For polymerizations of TVOS this precipitation procedure ensured quantitative transformation into the corresponding poly(vinyl alcohol) as we have described previously.[25]

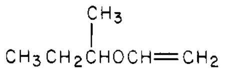
Characterization of Polymeric Products. Optical rotatory measurements were performed in benzene or toluene solutions (c 1-3 g/dL) at 25 °C by a Perkin-Elmer Model 141 spectropolarimeter with sensitivity ±0.003°. ^{1}H-NMR spectra were determined on a Jeol JNM-PS-100 at 30 °C. IR spectra were recorded on a Perkin-Elmer Model 225 spectrophotometer on liquid films or KBr pellets. Number average molecular weights ($\overline{M}_n$) were determined either in toluene solution using a membrane osmometer or in benzene using a Mechrolab vapor pressure osmometer.

Results and Discussion

Polymerization of (S)-1-methylpropyl vinyl ether (BVE)



MVE



$CH_3CH_2CH(CH_3)OCH{=}CH_2$

BVE

$(CH_3)_3SiOCH{=}CH_2$

TVOS

and (−)-menthyl vinyl ether (MVE) initiated by tropylium hexachloroantimonate in CH_2Cl_2 was studied at several temperatures. Data for polymer yields, molecular weights, and optical rotations are given in Tables I and II. IR and ^{1}H-NMR spectra are in agreement with a regular head-to-tail insertion of monomeric units. In the case of poly(BVE) ^{13}C-NMR spectra indicate that no racemization of the asymmetric carbon atom present in the monomer occurs during the polymerization.

From Table I it can be seen that, under conditions favoring propagation by free cationic species, MVE gives rise to polymers (unfractionated) having values of $[\alpha]^{25}_D$ very similar to the maximum value (~220°) reported in the literature for the most stereoregular sample obtained by low-temperature polymerization with $BF_3{\cdot}OEt_2$[24] or $EtAlCl_2$.[25] X-ray crystallographic studies of poly(MVE) have shown that a polymer with $[\alpha]^{25}_D$ − 165°, obtained from monomer having a lower optical purity (94%) than in the present work, is mainly isotactic.[12] The values of $[\alpha]^{25}_D$ now reported are essentially independent of temperature at least in the range examined −30 to +30 °C and the conclusion must be that isotactic poly(MVE) is produced with *only* the stereoregulating control exerted by freely growing solvated cationic chain ends and the incoming monomer. It follows therefore that use of complex catalysts and/or heterophase systems are not essential requirements at least for the formation of isotactic poly(MVE). It is conceivable that propagating systems under the influence of counterions or heterophase surfaces could also enhance or even oppose stereoregulating effects apparently arising only from steric interactions between solvated growing chains and monomeric MVE.

To conclude that the very high values of $[\alpha]^{25}_D$ found for poly(MVE) imply isotactic polymers, is only justified by analogy with the rotatory properties of similar materials reported in the literature. However, the large enhancement of optical activity unambiguously indicates a high degree of main chain regularity and it would be an amazing coincidence if the syndiotactic form of poly(MVE) gave rise to the same sign and magnitude of $[\alpha]^{25}_D$ as found for the isotactic polymer. As far as we are aware there is no published report of optical enhancement in a syndiotactic polymer obtained from chiral monomer. One reason might be that syndiotactic polymers mainly adopt planar zig-zag conformations.

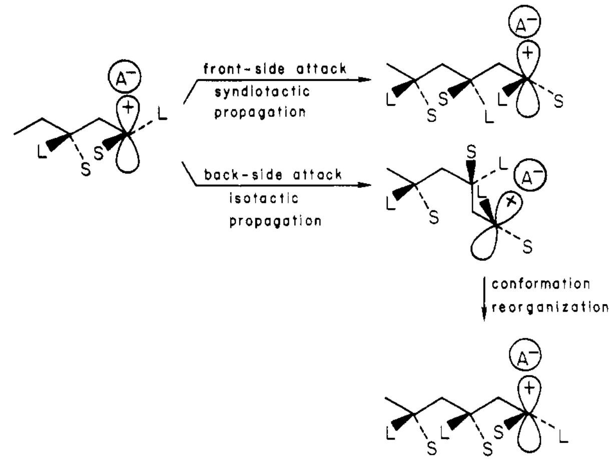
By comparison with MVE, the data of Table II show that polymerization of (S)-1-methylpropyl vinyl ether (BVE) carried out in the same experimental conditions reported for MVE gives polymeric products having optical rotations which are approximately one half of the average value (+300°) reported for a fractionated, highly isotactic sample.[13,14,21] Values of $[\alpha]^{25}_D$ reported in the present work relate to unfractionated materials which, however, are completely soluble in acetone and hence cannot contain any highly isotactic poly(BVE).[13] Nevertheless, the degree of enhancement of optical rotation observed (approximately five times that of the appropriate low molecular weight model compound)[13] is indicative of a degree of steric control in the propagation reaction.[31] Such a comparison illustrates the substantially greater asymmetric inductive influence of the (–)-menthyl group over that of the *sec*-butyl group during insertion of the monomer onto the growing chain end. Therefore, it must be concluded that the much more stereoregular fraction of poly(BVE), obtained by polymerization with the heterogeneous Vandenberg catalyst, arises from a propagation process assisted (in a stereochemical sense) by either a complex counterion and/or, more probably, by the catalyst surface. In this context it is interesting to note that poly(BVE) produced by polymerization with $EtAlCl_2$ in toluene at –78 °C gives a most stereoregular fraction having $[\alpha]^{25}{}_D + 245°$, intermediate between the products of the fully heterogeneous Vandenberg catalyst system and the fully homogeneous polymerizations observed in the present work.[21]

Under the same experimental conditions reported for MVE and BVE, trimethylvinyloxysilane (0.2–1.0 M) initiated by $C_7H_7SbCl_6$ ($0.1–2.0 \times 10^{-4}$ M) gave poly(vinyl alcohols) in recovered yields ranging from 30–40% as the reaction temperature was varied in the range –30 to +30 °C. All samples of poly(vinyl alcohol) recovered exhibited ^1H-NMR spectra in dimethyl sulfoxide solution and infrared spectra which were very similar to those described in the literature[25–27] for poly(vinyl alcohols) derived from poly(*tert*-butyl vinyl ether) and poly(TVO). Analysis of the NMR spectra indicated not less than 75% degree of syndiotacticity.

The earliest attempts[2,28] to explain stereoregulation in cationic polymerization of alkyl vinyl ethers assumed that stereocontrol originated via a transition state involving internal ring formation by alkoxy substituents in the polymer chain and the growing carbocation and predicted that isotactic polymers will result in all cases in agreement with experimental results for methyl, isopropyl, and isobutyl vinyl ethers.[2,5] However, it later became apparent that alkyl vinyl ethers having bulky substituents such as *tert*-butyl vinyl ether[26] and trimethylvinyloxysilane[27] yielded syndiotactic polymers when polymerized in relatively polar solvents, and isotactic polymers when polymerized with the same catalysts and reaction conditions in toluene. Although bulky groups such as *tert*-butyl and trimethylsilyl would be expected to exhibit the most pronounced degrees of stereoregulation in the growth process, the change from isotactic to syndiotactic placements, according to solvent, cannot be accounted for on steric grounds and indicates steric control by factors other than those assumed in the early mechanisms.[2,28]

Kunitake and Aso[29] proposed that the really important factor in controlling stereochemistry of chain growth in alkyl vinyl ether polymerization is the degree of association of growing cation and counterion. The physical size of the counterion would also be important but in a less dramatic way. Thus, as illustrated below, steric hindrance of bulky substituents of terminal and penultimate monomer units may be minimized and, assuming a planar carbocation, attack of monomer on the same side as the counterion (front side attack) leads to mainly syndiotactic placements. With the same polymer chain configuration, attack of monomer on the side opposite to the counterion (backside attack) leads to mainly isotactic placements. This simple model suffices to explain most of the existing experimental observations and differs from that generally assumed for propagating free radicals only in the effects of counterion. Nonpolar solvents such as toluene would be expected to favor tight association of the propagating cation and its counterion and hence favor backside attack with formation of isotactic polymer. Polar solvents such as CH_2Cl_2 would stabilize more separated ion pairs and favor frontside attack (thus minimizing steric repulsion between bulky groups present in monomer and the growing polymer chain) with formation of syndiotactic polymer.

Scheme I
Effect of Ion Pairing on Stereochemistry of Propagation for Alkyl Vinyl Ethers[29]



L = larger substituent
S = smaller substituent

These general predictions are both supported and qualified by the present results which, in essence, involve polymerization of alkyl vinyl ethers with bulky substituents under conditions where the counterion cannot exercise any influence on the growth reaction.

Considering first the polymerization of trimethylvinyloxysilane (TVOS), propagation via free ions would be predicted to involve the equivalent of exclusively frontside attack, so as to minimize steric interactions and lead to syndiotactic polymer, as observed experimentally, and consistent with other cationic polymerizations of this monomer in dichloromethane.[27]

Putting aside effects of chirality, menthyl vinyl ether (MVE) might be regarded as having an even bulkier substituent that TVOS and hence would be expected to yield mainly syndiotactic polymer by free-ion propagation. In reality the product of free-ion polymerization of (–)MVE is a highly isotactic polymer whose apparent stereoregularity does not vary as the temperature of polymerization is varied in the range –30 to +30 °C. Thus it is clear that the chiral influence present in (–)-menthyl vinyl ether is more important in controlling main chain stereoregularity than the more general bulkiness of the monomer substituent. It is not absolutely clear why isotactic polymer should be favored in this way but it must be presumed that the chiral influence of one or more monomer units in the growing chain supplies a powerful asymmetric influence in the transition state leading to incorporation of an additional chiral monomer. Such a high degree of stereoregulation in a truly homogeneous system has not previously been reported[1] although attention is drawn to the preference for formation of isotactic polymer in free-radical polymerization of triphenylmethyl methacrylate.[30]

The polymerization of (*S*)-1-methylpropyl vinyl ether (BVE) presents an intermediate case in terms of the bulky nature of the monomer substituent. Here the polymeric product has an optical rotatory power consistent with an apparent isotacticity approximately one-half of that which may be obtained with the best heterogeneous stereoregular catalysts. It would appear that, as expected, the chiral influence of the (*S*)-1-methylpropyl substituent is significantly less than that of the corresponding (–)-menthyl group. These results, although very limited in scope, suggest that the influence of chiral substituents might be significant in other types of polymerization and related studies could be useful in understanding details of the chain propagation processes.

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(31) In studies of the optical rotatory power of polymers prepared from chiral monomers it is usually found that unfractionated samples give a low indication of the degree of main-chain stereoregularity. The present results must, therefore, be taken as only a crude measure of the chiral influence of the (*S*)-1-methylpropyl group. Again it must be admitted that syndiotactic placements could give rise to enhancement of optical activity but as far as we are aware there is no evidence for this.

Active Center Determination in Ziegler–Natta Polymerization. Interference by Tritium Exchange Reactions in the Tritiated Alcohol Quench Method

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ABSTRACT: The occurrence of polymer labeling via tritium exchange reactions has been demonstrated under the conditions normally employed for tritiated alcohol quenching of Ziegler–Natta polymerization systems. The efficiency of the exchange is dependent upon the nature of the catalyst, cocatalyst, monomer, and solvent. The possible interference of such reactions in the determination of active center concentrations is discussed.

The tritiated alcohol quench method, originally developed by Feldman and Perry,[1] has been very widely used[1-10] for determining the number of active centers in Ziegler–Natta polymerization. Addition of hydroxy-tritiated alcohols to the polymerization reaction leads to destruction of the catalytically active organometallic species and simultaneous labeling of the bound polymer chain (eq 1). Determination of the number of labeled

$$\mathrm{Cat}^{+-}\mathrm{CH}_2\!\sim\!\sim\mathrm{P} + \mathrm{ROT} \rightarrow \mathrm{Cat\text{-}OR} + \mathrm{TCH}_2\!\sim\!\sim\mathrm{P} \tag{1}$$

polymer molecules permits the calculation of the active center concentration. Complications arise since non-propagative metal polymer bonds are also labeled and a kinetic isotope effect is operative; however, both of these difficulties may be overcome by appropriate techniques.[7]

A serious drawback of all radiotracer methods, including the above, is a lack of precise knowledge as to the nature of the incorporated radioactivity. In the above method it is necessary to assume that tritium is only incorporated into the polymer by the quench reaction cited (eq 1) and that extraneous radioactivity may be efficiently removed. Whereas the latter may be confirmed by repetitive purification procedures, it is difficult to draw unequivocal conclusions about the former. The assumption would appear sound in the absence of any alternative reaction pathway for tritium labeling of the preformed polymer.

However, tritium exchange reactions catalyzed by Lewis acids such as $AlCl_3$ are well known in the literature,[11] and while used principally for labeling aromatic compounds, exchange of aliphatic protons has been reported.[12] Since typical Ziegler–Natta catalyst formulations involve the use of Lewis acids, it seemed pertinent to investigate the possibility of such tritium exchange reactions occurring with preformed polymer, on quenching with tritiated

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