section of the PHV reciprocal lattice, the molecular chains in the crystal are perpendicular to the surface of the crystalline lamellae. The diffractogram also confirmed the *pgg* symmetry since only even-order reflections are observed along ($h00$) and ($0k0$) directions. Furthermore, this confirms the orthorhombic $P2_12_12_1$ space group for the chiral PHV, the same as proposed by the X-ray analysis[8] for the racemic polymer.

In conclusion, the crystallographic results for the naturally occurring optically active PHV by X-ray diffraction and electron diffraction are in good agreement. The unit cell parameters for the optically active and racemic PHV are the same except for a significant disagreement in the *a* parameter. From the results presented here, it also appears that the heteropolymer is a physical mixture of PHV and PHB. Since activated sewage sludge was the source of the heteropolymer,[13] it may be assumed that different bacterial species were present, some of which produced PHV and others PHB. A true copolyester of β-hydroxyvalerate/β-hydroxybutyrate from a homogeneous bacterial culture has been reported.[14]

Registry No. PHV, 67291-18-3; PHB, 26744-04-7; β-hydroxyvaleric acid homopolymer, 83120-66-5; β-hydroxybutyric acid homopolymer, 26063-00-3.

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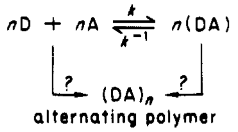
Monomer Orientation Control by Donor–Acceptor Complex Participation in Alternating Copolymerization

Alternating copolymerization of certain pairs of vinyl monomers has been known for many years, and debate and disagreement about the mechanism of this process have been extensive.[1,2] The probability of formation of such regularly alternating copolymers via a random process is very low. However, one set of properties invariably associated with monomer pairs that exhibit this alternating tendency is the complementary electron-donor/electron-acceptor character of the pair. A strongly electron-donating monomer (D) tends to undergo alternating copolymerization with a strongly electron-accepting monomer (A). Thus, two independent theories have been advanced to account for this result. The first postulate[3] was that polarity differences between the radical chain end and the incoming monomer would lower the energy of activation of cross-propagation, as opposed to a homopropagation reaction, thus producing strictly alternating copolymers when the comonomers have widely different polarities. The second postulate[4] was that an electron-donating/electron-accepting monomer pair formed a donor–acceptor complex (DA) that, due to an inherently higher reactivity of the complex relative to the free monomers, preferentially added to the chain end:[5–9]



(1)

The most convincing evidence for participation of DA is that the overall rate of polymerization (R_p) is maximum at a monomer composition ratio of nearly 1:1, where the concentration of DA ([DA]) is greatest. However, the rate maximum seldom occurs at exactly 1:1. Also, R_p at constant monomer ratio is generally greater than first order in total monomer concentration, $[M]_T$, inconsistent with cross-propagation. In spite of the large amount of data available, there is still disagreement regarding the exact mechanism. The actual [DA] in systems that show an alternating tendency is invariably low (K's are generally 0.01–0.5). Thus, if DA is involved in the propagation step, it must have high reactivity relative to the free monomers. This point is still open to debate as well.

In previous studies, predominantly kinetic and polymer composition data have been used to draw conclusions. Both techniques are subject to considerable error. Thus, it is important to have reliable data to distinguish between such mechanistic subtleties as DA formation prior to addition and complex formation with the chain end.

We considered that some innovative source of data was needed to resolve the question. According to Mulliken,[10] a DA is expected to have a preferred geometry; thus, a DA may add to the chain end in a concerted manner (as opposed to stepwise addition of D and A), introducing controlled stereoregularity. If the "free" monomers add to the chain end, random stereochemistry would be expected.[11] A study of copolymer structure and stereochemistry as a function of copolymerization conditions was thus undertaken. Conditions were used so as to shift the DA equilibrium one way or the other. The system *N*-phenylmaleimide (NPM)–2-chloroethyl vinyl ether (CEVE) was selected. NPM is an acceptor monomer with an *e* value of +3.24.[12] CEVE is a donor monomer with an *e* value of −1.58.[12] The objective was to determine whether or not DA participates significantly in the propagation step. ^{13}C NMR spectroscopy was used extensively for the determination of the stereoregularity. Copolymer epimerization studies and comparison of copolymer ^{13}C NMR chemical shifts with those of stereospecific model compounds indicated that the stereochemistry at the succinimide units in the copolymer was predominantly cis. Copolymerization conditions that were expected to enhance the fraction of

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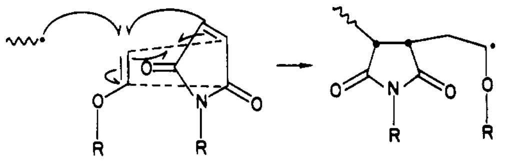
NPM in DA (e.g., low temperature, excess vinyl ether, "inert" solvent, higher total monomer concentration, and stronger DA character of the comonomer pair) yielded copolymers that possessed a higher cis:trans ratio.[13-15]

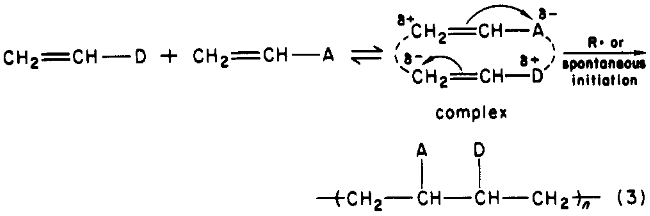
The preference for cis stereochemistry observed was opposite to what would be expected if the mechanism had involved consecutive alternate monomer additions. If the "free monomer" mechanism had been operational, succinimide unit stereochemistry would have been predominantly trans, and stereochemical variations would have been opposite to that observed. The observed results are nicely accommodated by the "complex" mechanism (eq 2).



(2)

Thus, it was proposed that succinimide unit stereochemistry is dependent on the fraction of NPM monomer in DA and that DA participates in the propagation steps. These results provide the first evidence for stereochemical control in copolymerization of a D monomer and an A monomer. The stereochemistry of the vinyl ether unit was random, as expected.

Also inherent in the concept of participation of a DA in alternating copolymerization of a pair of vinyl monomers, both of which are unsymmetrical, is orientation control of the monomers in the developing polymer chain (eq 3):



Thus, radical attack on the complex, followed by a concerted pathway to simultaneously incorporate both monomers into the propagating chain, would be predicted to lead to orientation control on the basis of charge separation in the individual components of DA. Again, theory[10] predicts that the maximum amount of stabilization of DA is attained if the complex conformation is that in which maximum overlap occurs between the HOMO of the donor and the LUMO of the acceptor. Such a structure, represented qualitatively in eq 3, is predicted to produce alternating copolymers having head-to-head–tail-to-tail sequences rather than the conventional head-to-tail structure predicted by free monomer initiation and propagation.

We would now like to report the results of our recent experiments designed to test the latter prediction, which, for the first time, show that indeed head-to-head–tail-to-tail sequences can be introduced into the copolymer chain from a suitably selected monomer pair.

Orientation control in radical-initiated homopolymerization of a vinyl monomer is generally considered to be the result of radical stability and steric factors, both of which predict a head-to-tail structure.[16] Alternating copolymerization of the comonomer pair *N*-phenylcitraconamide (NPC) and CEVE has been studied, and on the basis of monomer polarities and the predicted orientation of the monomer in DA, the predicted structure of the copolymer is that represented by abc rather than by a′b′c′ (eq 4). The copolymer was prepared at 60 °C, using AIBN as initiator, at total monomer concentration, M_T = 0.535, and mole fraction of A, χ_M = 0.467. Figure 1 shows the ^{13}C NMR spectrum of the copolymer, which is clearly structure abc, based upon a comparison of the chemical shifts of this copolymer with those of the corresponding *N*-phenylmaleimide (NPM)–CEVE copolymer.[13-15]

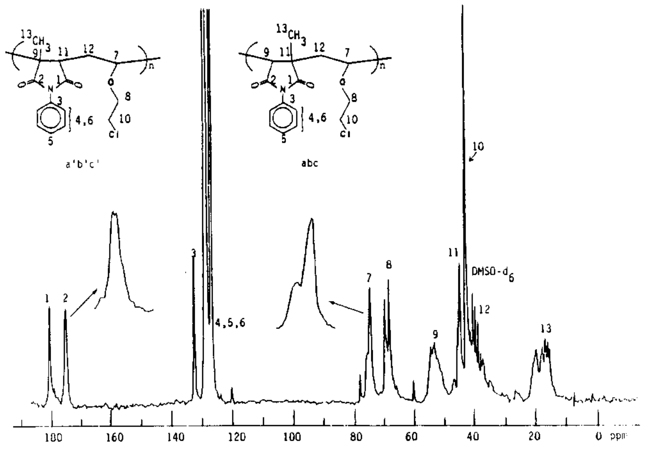
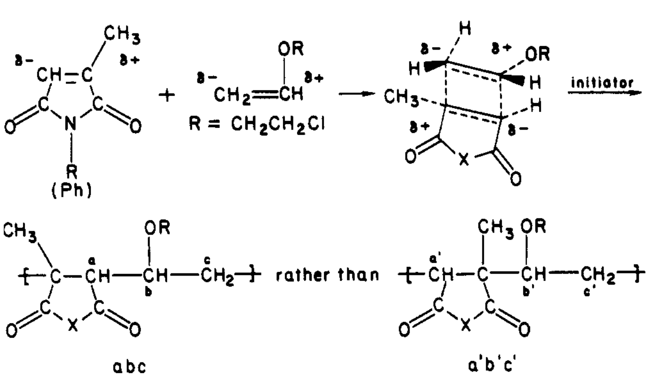


Figure 1. ^{13}C NMR spectrum of *N*-phenylcitraconimide–CEVE copolymer.



(4)

The resonances corresponding to carbons 1, 9, 11, and 12 in the NPC–CEVE copolymer appear downfield from the corresponding ^{13}C resonances in the ^{13}C NMR spectrum of the NPM–CEVE copolymer, whereas carbons 2, 7, and 8 appear at higher field in the NPC–CEVE copolymer. These observations are consistent only with the structure abc. This follows from the fact that the methyl group in abc is γ to the methine carbons of adjacent vinyl ether units and carbonyl 2, but either α or β to carbons 1, 9, 11, and 12. Such is not the case for structure a′b′c′. The ^{13}C chemical shift of carbon 10 is approximately the same in both copolymers.

However, in the case of NPC–CEVE copolymerization, steric control and polarity control are predicted, according to DA theory, to lead to the same copolymer, since the methyl group is electron-donating. Thus, to test the prediction further we synthesized two dialkyl cyanoethylene dicarboxylates[17] (Scheme I) and studied their copolymerization with CEVE. Figure 2 shows the ^{13}C NMR spectrum of the DMCE–CEVE copolymer in which both orientations of CEVE in the copolymer are clearly discernible. Figure 3 shows the ^{13}C NMR spectrum of the DECE–CEVE copolymer, which again clearly shows the presence of both copolymers, even though the temperature of polymerization was 60 °C. In order to more definitely identify the critical carbon atoms of the chain of the latter copolymer, a multiplicity sequence spectrum (INEPT[18]) was obtained (Figure 4), which clearly identifies critical carbon atoms (1,1′ = –C–, negative intensity; 2,2′ = –CH, positive intensity; 3,3′ = –CH, positive intensity; 4,4′ = –CH$_2$–, negative intensity). The assignments of the

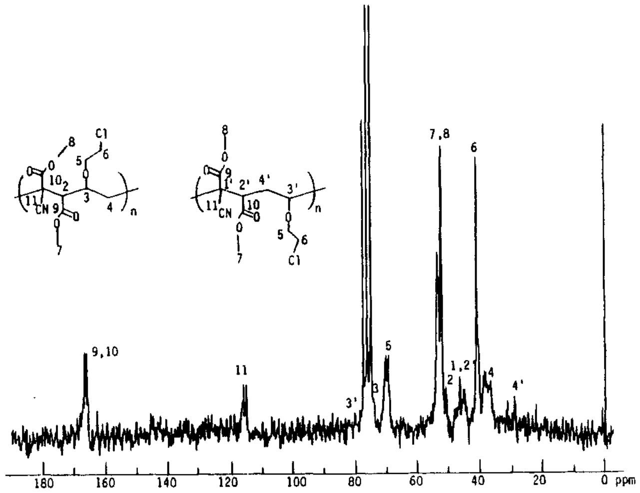


Figure 2. 25-MHz noise-decoupled ^{13}C NMR spectrum of a DMCE–CEVE copolymer obtained in $CDCl_3$ at room temperature.

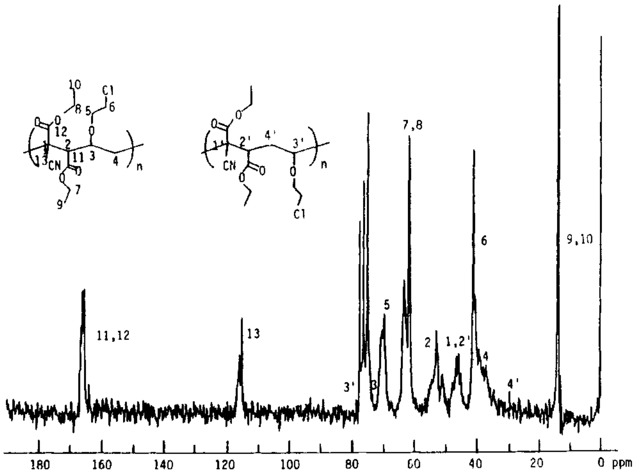
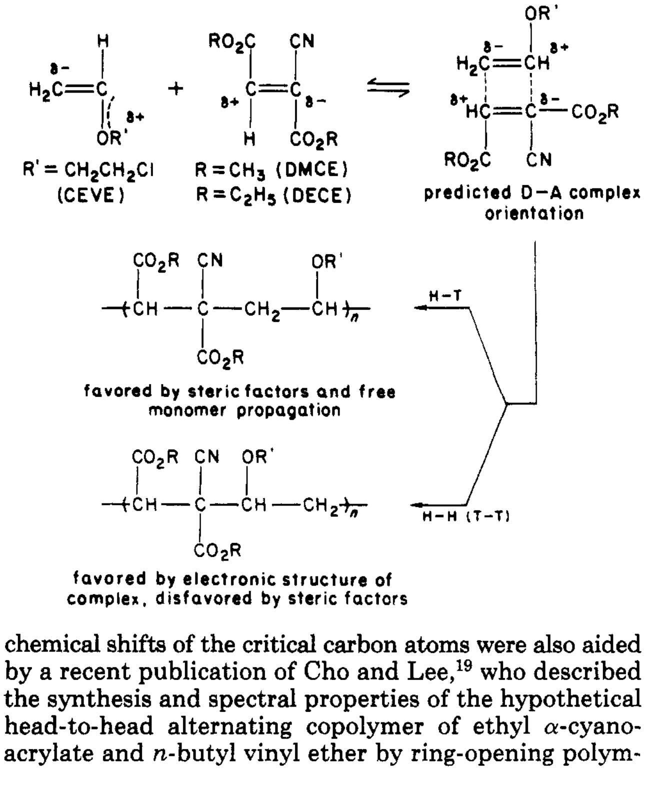


Figure 3. 25-MHz noise-decoupled ^{13}C NMR spectrum of a DECE–CEVE copolymer obtained in $CDCl_3$ at room temperature.

Scheme I



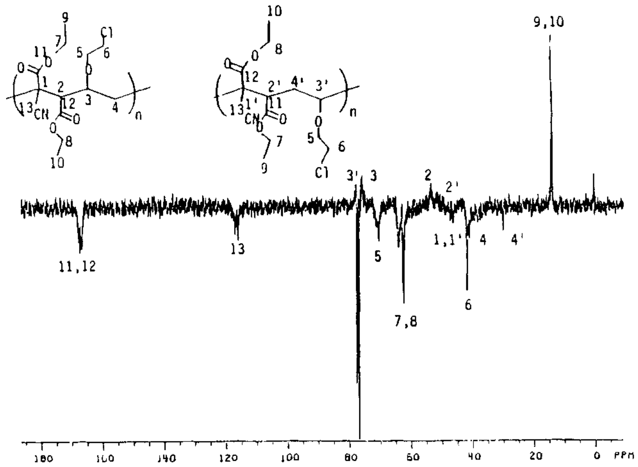


Figure 4. 75-MHz multiplicity ^{13}C NMR spectrum of a DECE–CEVE copolymer obtained in $CDCl_3$ at room temperature.

chemical shifts of the critical carbon atoms were also aided by a recent publication of Cho and Lee,[19] who described the synthesis and spectral properties of the hypothetical head-to-head alternating copolymer of ethyl α-cyanoacrylate and n-butyl vinyl ether by ring-opening polymerization of 2-n-butoxy-5-cyano-6-ethoxy-3,4-dihydro-2H-pyran.

On the basis of this initial evidence, it can be predicted that the experimental parameters that were shown to increase the cis:trans ratio of the NPM unit in the copolymer reported in our earlier papers[13-15] (e.g., lower temperature, excess donor, "inert" solvent, higher total monomer concentration, and stronger donor–acceptor character of the comonomer pair) would also increase the ratio of the head-to-head copolymer in these systems. Further work along these lines is in progress.

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Registry No. (CEVE)·(NPC) (copolymer), 91631-66-2; (CEVE)·(DMCE) (copolymer), 91631-67-3; (CEVE)·(DECE) (copolymer), 91631-69-5; (CEVE)·(NPM) (copolymer), 91631-70-8.

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Polymerization of Vinylidene-d_2 Fluoride. Minimal Regiosequence and Branch Defects and Assignment of Preferred Chain-Growth Direction from the Deuterium Isotope Effect

Poly(vinylidene fluoride) has attracted considerable research and technological interest, mainly due to its piezoelectric and pyroelectric behavior.[1] The properties of the polymer (commonly abbreviated as PVF_2) depend on its chemical microstructure, which could be represented as $(-CH_2-CF_2-)_n$ for an ideal, defect-free material (neglecting end groups).

It is well established that the free-radical addition polymerization of VF_2 is not regiospecific.[2] Typically 5% of monomer units enter the growing chain with a reverse orientation creating anomalous head–head ($-CF_2-CF_2-$) and tail–tail ($-CH_2-CH_2-$) junctions.[3] These anomalous structures must exert some influence on the properties of PVF_2.[4] Therefore it would be desirable to prepare a perfectly head-to-tail (isoregic) PVF_2 for comparison with commercial samples, in which the level of reversed units varies over a limited range of only 3.5–6%.[1]

However, it seems unlikely that this small range of regiosequence defects can account for the variation in properties of commercial PVF_2 materials. We postulate that the number and type of chain branches present exert an equal if not greater effect on the chemical and physical properties of PVF_2. Unfortunately this branch structure is not as easy to characterize as the regiosequence structure, so we attempt to eliminate its effect here by preparing a highly linear polymer.

The frequency of monomer reversals during VF_2 polymerization is greater at higher temperature,[5] but it is not practical to eliminate their occurrence by going to low temperatures.[6-8] We have published an alternative procedure for preparing pure isoregic PVF_2 by the reductive dechlorination of the precursor polymer poly(1,1-dichloro-2,2-difluoroethylene).[9] In practice this material could not be obtained with a molecular weight of sufficient magnitude to impart typical polymeric properties, thus obviating a meaningful comparison with commercial PVF_2 samples.

We disclose here a method for obtaining high-molecular-weight PVF_2 with only 2.84 ± 0.02% of reversed monomer units, which is the lowest value yet reported. The method involves the bulk polymerization of 1,1-dideuterio-2,2-difluoroethylene (VF_2-d_2) at 0 °C with trichloroacetyl peroxide initiator. We believe this is the first report of an isotope effect on polymer sequence distribution. Also, since deuteration of the polymer exerts a primary isotope effect on the rate of hydrogen transfer,[10] the frequency of chain branching is reduced. Thus our samples of PVF_2-d_2 are less branched than commercial materials and more stable toward dehydrofluorination. The higher stability results from fewer labile sites containing tertiary hydrogen at branch points, and the isotope effect on hydrogen fluoride elimination.

The perdeuterated monomer VF_2-d_2 was synthesized by the procedure of Edgell and Ultef.[11] Trifluoroethanol-d_3 (99 atom % D minimum) was purchased from Merck, Sharp, and Dohme and reacted with *p*-toluenesulfonic acid. The ester derivative was then treated with sodium iodide to liberate CF_3CD_2I. The purified CF_3CD_2I was dropped slowly onto Mg in ether, and the evolved $CD_2{=}CF_2$ was collected and then transferred to a vacuum line where it was freeze–thaw degassed and distilled. The overall yield was 44%. The isotopic purity of the monomer was checked by mass spectrographic analysis. The composition by mole percent was as follows: $CD_2{=}CF_2$, 99.28; $CDH{=}CF_2$, 0.68; $CH_2{=}CF_2$, less than 0.04.

Table I
Properties of PVF_2-h_2 and PVF_2-d_2 Prepared in Bulk at 0 °C with Trichloroacetyl Peroxide Initiator

sample	monomer	initiator concn, mol %	T_m,[a] °C	$[\eta]$,[b] dL/g	ρ,[c] g/mL	% reverse addition
A-h_2	$CH_2{=}CF_2$	1	180.9	0.45	1.792	3.45
B-h_2	$CH_2{=}CF_2$	0.1	179.5	2.6	1.770	3.46
C-d_2	$CD_2{=}CF_2$	1	185.1	2.8	1.840	2.86
D-d_2	$CD_2{=}CF_2$	0.1	188.3	4.1	1.860	2.83

[a] First melting point of nascent material measured by DSC. Subsequent melting temperatures were always several degrees lower. [b] Intrinsic viscosity measured at 125 °C in dimethylformamide. Under these conditions the intrinsic viscosities of commercial polymers (Kureha, Kynar, Solef, and Pennwalt) are typically around 1.0.[16] [c] Density of polymer melt pressed into 3-mm-diameter disk of 1-mm thickness and rapidly quenched to room temperature.

The polymerization initiator was trichloroacetyl peroxide, which was prepared from trichloroacetyl chloride and sodium peroxide according to standard procedure.[12] It was added to heavy-wall Pyrex ampules as a solution in 1,2-dichlorotetrafluoroethane, which was then evaporated to dryness at −80 °C. The monomer was then condensed into the tube at −196 °C. The tube was sealed and rapidly warmed to the polymerization temperature of 0 °C in a pressurized reactor which was held in an ice–water bath. Control samples with the protonated monomer $CH_2{=}CF_2$ were prepared in an identical manner.

After a suitable polymerization time had elapsed the tubes were frozen in liquid nitrogen and cut open. The recovered polymers were extracted with acetone to remove initiator residue and possible traces of oligomers and dried in a vacuum oven. The polymers were examined by NMR with a JEOL GX-500 spectrometer. Fluorine-19 spectra were recorded at 470.6 MHz using 5% by weight polymer solutions in dimethylformamide-d_7 at 25 °C. The spectra were analyzed according to our previously published procedure.[13]

Some properties of the PVF_2-h_2 and PVF_2-d_2 samples are compared in Table I. We note that the molecular weights of the deuterated samples, as reflected by their intrinsic viscosities, are significantly higher than their protonated analogues. This fact most likely results from the primary kinetic isotope effect on transfer and disproportionation reactions. We calculate $\bar{M}_v$ values of 11.9×10^6 and 20.1×10^6 for PVF_2 samples C-d_2 and D-d_2 using the literature Mark–Houwink–Sakurada constants.[14] The viscosity measurement overestimates molecular weights for PVF_2,[5,15] but it is clear that the deuterated samples have extremely high degrees of polymerization so that end groups will not interfere with our NMR analysis.

The densities of the deuterated polymers are higher as well, but most of the difference arises from the larger mass of deuterium. However the densities are still larger after correcting for this than those of commercial PVF_2 samples (e.g., 1.80 corrected for D-d_2 vs. 1.78 for Kureha 1100), suggesting a higher degree of crystallinity and therefore

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