undergoes a significant decrease in going from the neat liquid to an aqueous solution. This happens in spite of the fact that the band moves to a higher frequency, which indicates an increase in the gauche bond concentration. Therefore we might have expected an increase in bandwidth. Detailed infrared studies of Matsuura and Fukuhara indicate that POM_2 is more ordered in dilute solution than as a neat liquid,[5] and this accounts for the observed D-LAM band narrowing.

In summary, our measurements suggest that vibrational spectroscopic measurements in the low-frequency region can provide information on *long-range* conformational disorder in highly disordered chain systems.

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Registry No. polybutadiene, 9003-17-2; squalene, 111-02-4; poly(ethylene oxide), 25322-68-3; poly(tetramethylene oxide), 25190-06-1; poly(ethylene terephthalate), 25038-59-9; squalane, 111-01-3.

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R. G. Snyder*
Department of Chemistry
University of California
Berkeley, California 94720

S. L. Wunder
E. I. du Pont de Nemours and Co.
Wilmington, Delaware 19898

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Blends of Homo- and Copolymers of Ethylene and Vinyl Chloride: A Compatibility Study

We have recently[1] obtained a complete series of ethylene-vinyl chloride (E-V) copolymers through the reductive dechlorination of poly(vinyl chloride) (PVC) with tri-*n*-butyltin hydride. ^{13}C NMR spectroscopy was utilized to determine the microstructures of these E-V copolymers, including their comonomer compositions, their sequence distributions, and the stereosequences of neighboring V units. Solid-state and solution measurements[2,3] performed on these E-V copolymers have demonstrated a remarkable sensitivity of their physical properties to their microstructures.

We have begun to study the blend properties of these E-V copolymers. In this communication we report on our initial studies of the compatibility of E-V copolymer blends, using differential scanning calorimetry (DSC) as a probe of blend compatibility.

Blends were made by casting films from dilute solutions (1-2 wt %) composed of equal volumes of E-V copolymers or their constituent homopolymers PVC and polyethylene (PE). For blends with amorphous E-V copolymers and PVC, tetrahydrofuran was used as the casting solvent, while toluene was employed for the crystalline E-V copolymers and PE. The blend films were cast in a poly(tetrafluoroethylene) trough and, after ambient drying, were removed and dried further in a vacuum oven for 1 h at 90 °C to remove residual solvent.

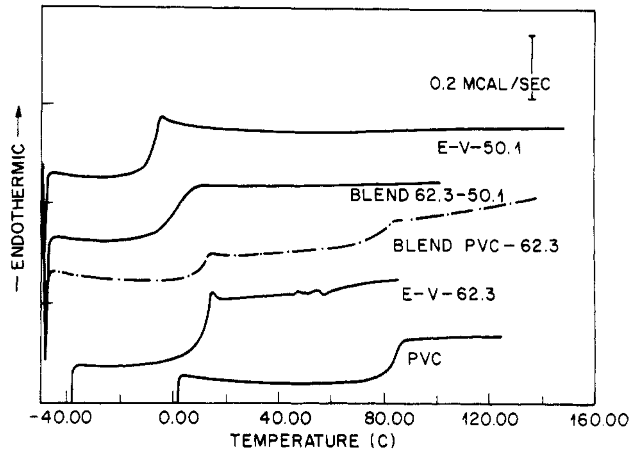

Figure 1. DSC scans for PVC, E-V-62.3, E-V-50.1, 100-62.3 blend, and 62.3-50.1 blend.

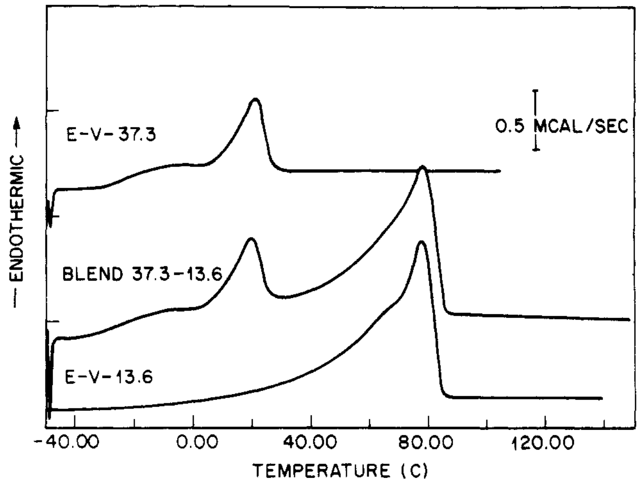

Figure 2. DSC scans for E-V-13.6, E-V-37.3, and 37.3-13.6 blend.

DSC scans were recorded for all the individual E-V copolymers, PVC, PE, and their blends on a Perkin-Elmer Model DSC-4. Sample sizes ranged from 6 to 16 mg and a fixed heating rate of 10 °C/min was employed throughout. Illustrative DSC traces are shown in Figures 1 and 2 for several of the E-V copolymers and their blends.

Glass transition temperatures (T_g) are defined as the midpoints of the transitions in the DSC scan, while melting temperatures (T_m) are identified with the maxima of the fusion endotherms. T_g's and T_m's observed for the blends and their constituents are reported in Table I. The final column in Table I indicates the compatibility (C)/incompatibility (I) of each blend based on a comparison of the T_g's and T_m's observed for the blends and their individual components. For blends composed of two amorphous components, observation of a single T_g(blend) intermediate between the T_g's (T_{g1}, T_{g2}) of the components is taken as proof of compatibility. Blends with at least one crystalline component are designated incompatible if the T_m's and T_g's of the blend and the pure crystalline and amorphous components are the same.

These initial compatibility measurements performed on 50/50 (v/v) blends of E-V copolymers are summarized in Figure 3. All blends with at least one crystalline component (<37.3 mol % V) are found to be incompatible, while those composed of two amorphous components are compatible only when their compositions differ by less

Table I
T_g, T_m, and Compatibility of E-V Copolymer Blends

E-V copolymer blend	T_{g1}	T_{g2}	T_{m1}	T_{m2}	T_g(blend)	T_m(blend)	compatibility
100-85.3	83	42			49		C
100-84.3	83	54			70		C
100-62.3	80	12			77, 10		I
100-50.1	83	-8			81, -11		I
100-37.3	83	-26		21	79, -23	20	I
85.3-71.7	42	22			31		C
85.3-50.1	42	-8			45, -9		I
62.3-50.1	12	-8			0		C
50.1-37.3	-8	-26		21	-9, -24	21	I
37.3-21.2	-26	-39	21	54	-25, -39	21, 53	I
37.3-13.6	-26		21	78	-28	20, 78	I
37.3-0.0	-26		21	128	-25	21, 123	I
21.2-13.6	-39		54	78	-38	52, 79	I
13.6-0.0			78	128		77, 122	I

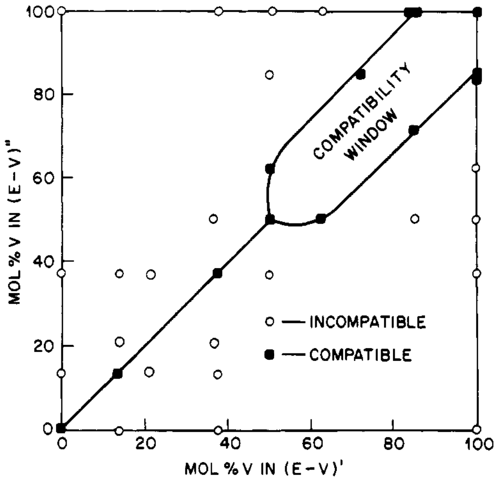

Figure 3. Compatibility diagram for E-V copolymer blends.

than 15 mol % V or E units. On the basis of the difference in solubility parameters (δ) of the constituent homopolymers,[4] i.e., $\delta(\mathrm{PVC}) = 9.4$-$10.8\ (\mathrm{cal/cm^3})^{1/2}$ and $\delta(\mathrm{PE}) = 7.7$-$8.35\ (\mathrm{cal/cm^3})^{1/2}$, it would seem fair to ask why any of the E-V copolymer blends are compatible.

Paul and Barlow[5] have used a binary interaction model for the miscibility of copolymers in blends to show that if there is any mismatch between the solubility parameters of the constituent monomers, then any difference in composition between the two copolymers should lead to incompatibility. This result applies in the limit that both copolymers have very high molecular weights. However, for finite molecular weights, where the combinatorial entropy of mixing still contributes to the free energy, they have also shown that some finite mismatch in copolymer composition can be tolerated. The critical composition difference ($\phi_2' - \phi_2''$) between two copolymers (indicated by single and double primes) for miscibility is given by Paul and Barlow[5] as $\phi_2' - \phi_2'' = [2\rho RT/M(\delta_1 - \delta_2)^2]^{1/2}$, where $M' = M'' = M$ is the molecular weight and $\rho' = \rho'' = \rho$ is the density.

Using $\delta_1 - \delta_2 = \delta(\mathrm{PE}) - \delta(\mathrm{PVC}) = (7.7$-$8.35) - (9.4$-$10.8)\ (\mathrm{cal/cm^3})^{1/2}$, $\rho = 1.2\ \mathrm{g/cm^3}$, and $M = 5 \times 10^4$ appropriate to our E-V copolymers, each of which is composed of 1000 repeat units,[1] we obtain a critical composition difference of 6-16 mol % V or E units. This is consistent with the compatibility observed for our blends of amorphous E-V copolymers differing by less than 15 mol % in composition.

Having seen that the relatively small compatibility window (see Figure 3) found for the amorphous E-V copolymer blends is likely due to the offset of dissimilar solubility parameters by the combinatorial entropy of mixing 1000 repeat unit chains, we can suggest a basis for the immiscibility of all E-V blends having at least one crystalline component. We know from our microstructural[1] and thermal[2] studies that three consecutive E units (-EEE-) is the minimum crystallizable sequence in E-V copolymers. Those E-V copolymers with fewer average numbers of consecutive E units are amorphous.

When amorphous and crystalline E-V copolymers are blended, the combinatorial entropy of mixing is not sufficient to overcome both the difference in solubility parameters and the free energy of crystallization that is lost by the crystalline component if a compatible blend is to form.[6] Hence, these E-V blends are incompatible. Apparently the combinatorial entropy of mixing is not even large enough to overcome the difference in the free energies of crystallization[7] between two blended crystalline E-V copolymers, because the resulting blend is incompatible, with each component phase forming separate crystals.

For example E-V-13.6 has an average of 6 consecutive E units, while PE has 1000 E units. The difference in the stability, or free energy, between the small, presumably micellar-like crystallites in E-V-13.6 and the much larger crystalline lamellae in PE is too great to be balanced by the combinational entropy of mixing, so their blend is incompatible, with each component crystallizing separately (see Table I). The free energy that would be lost by forcing PE into the small-crystal morphology of E-V-13.6, which is dictated by its microstructure, prevents the formation of a compatible blend even though their compositions differ by less than 15 mol %. Similar remarks apply to the other incompatible blends composed of two crystalline E-V copolymers, such as (E-V-37.3 + E-V-21.2) and (E-V-21.2 + E-V-13.6), whose compositions differ by ≤15 mol % but still form separate crystalline and amorphous phases as judged by the T_g's and T_m's observed for these blends.

We are presently searching for experimental probes of copolymer compatibility that will both complement our DSC studies and provide information concerning the size scale of mixing and the morphology of the incompatible blends. FTIR spectra have been recorded for each of the E-V copolymer blends and their constituents, and we are attempting to locate specific vibrational bands that are sensitive to and reflect the degree of mixing in these blends.

Registry No. PVC, 9002-86-2; PE, 9002-88-4.

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Trevor N. Bowmer
Bell Communications Research
Murray Hill, New Jersey 07974

Alan E. Tonelli*
AT&T Bell Laboratories
Murray Hill, New Jersey 07974

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Fluorescence Quenching in Pyrene/Benzil End-Labeled Poly(tetramethylene oxide). Cyclization Dynamics in Polymers. 19

Cyclization rates provide an important measure of the large-amplitude dynamics of polymer chains.[1,2] While these rates are not trivial to measure, reliable values of the rate constant k_1 for diffusion-controlled cyclization can be obtained from careful fluorescence quenching experiments on polymers of the form $F\sim\sim\sim Q$ containing a fluorescent group F on one chain end and a quencher group Q on the other.

While the fluorescence measurements themselves require great care, the most demanding aspects of the experiments are the synthesis and characterization of polymers of low molecular weight distribution (MWD) containing appropriate end groups. From the point of view of synthesis, it is much easier to obtain polymers with identical end groups.[3] This limits the choice of fluorescent dyes that can be used, since F* must have a suitably long lifetime and interact with F at the diffusion-controlled rate. These criteria are met by pyrene, whose derivatives have lifetimes of ca. 200 ns and which undergo diffusion-controlled excimer formation. In consequence, most of the experiments published describing cyclization dynamics have employed pyrene end groups and report rates of intramolecular pyrene excimer formation. The greatest effort has focused on polystyrene.[3a,b,4] The effect of chemical structure on cyclization rates is an important question. There is a particular interest in polymers more flexible than polystyrene, where in principle current techniques should permit one to study the end-to-end cyclization of longer chains. Two such polymers for which some cyclization rates have been reported are poly(ethylene oxide)[5] and poly(dimethylsiloxane).[6]

It was our hope to extend these studies to poly(tetramethylene oxide) (polyTHF). It is flexible, soluble in a wide variety of solvents, and amenable to synthesis from tetrahydrofuran by cationic living polymerization. One of the attractive features of the polymerization mechanism is that it seemed possible to use a derivative of one chromophore (F or Q) to initiate polymerization in order to obtain a polymer containing a specific group on one end and a functional group capable of further transformation on the other. In a polymer such as $Q\sim\sim\sim CH_2OH$, one can study cyclization by a variety of means depending upon which F group one attaches to the CH_2OH group. Here we report a brief outline of two syntheses of polyTHF molecules which satisfy these requirements and our initial results on measurements of cyclization rates by intramolecular fluorescence quenching studies. Full details of the synthesis will be reported elsewhere.

Scheme I

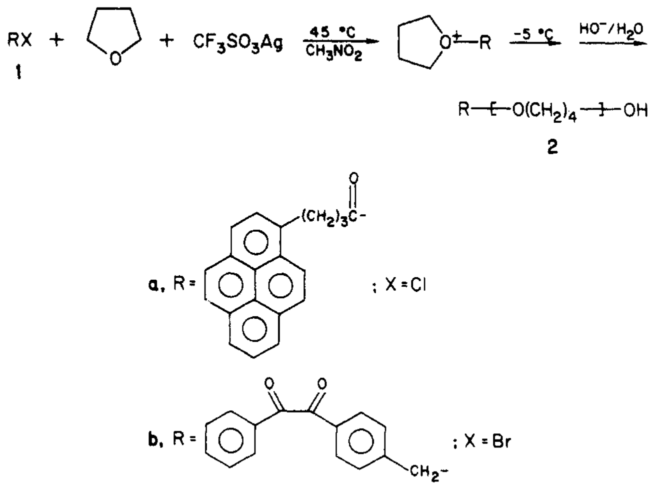

Table I
Characterization of PolyTHF Samples and Cyclization Rate Constants in Toluene at Room Temperature

sample	N[a]	M_n GPC	M_n UV[b]	M_w/M_n	τ, ns	$10^{-6}\langle k_1\rangle$, s^{-1}
Py-polyTHF-OH (2)		20100	24500	1.12	186.0	
Py-polyTHF-Bz (3)	740	10700	11300	1.15	162.6	7.8
Py-polyTHF-Bz (3)	440	6700	6800	1.08	140.3	17

other polymers	N	M_n (interpolated)[c]	$10^{-6}\langle k_1\rangle$, s^{-1}
Py-PDMS-Py	440	16400	23[d]
Py-polystyrene-Py	440	23000	0.29[e]
Py-polystyrene-Py	740	38000	0.05[e]

[a] Number of backbone bonds calculated from M_n [b] Based upon pyrene absorption. [c] Interpolated from previously reported values of $\langle k_1\rangle$ for various chain lengths. [d] Reference 6. [e] Reference 3a.

As shown in Scheme I, treatment of **1a** or **1b** with silver triflate in THF (7.8 M)/nitromethane at room temperature or below, using standard vacuum-line techniques, gave polymers of the form **2**, but with substantial polydispersities ($M_w/M_n \sim$ 1.3–1.5). When the initiation step was carried out at 45 °C, above the ceiling temperature for the polymer, and rapidly cooled to −5 °C, polymerization to low (ca. 10%) conversion produced polymer samples of acceptably low MWD ($M_w/M_n \sim$ 1.1). Two samples of **2b** were esterified with **1a** to produce polymers Bz-polyTHF-Py (**3**) with benzil (Bz) groups on one end and Py groups on the other. Characterization of the polymers, Table I, indicated quantitative benzil groups in **2b** and **3**, whereas **3** contained approximately 0.85 Py group per chain.

Benzil has a lower singlet energy than pyrene whereas pyrene has a much higher molar extinction coefficient at 345 nm. Irradiation of the dilute solutions **3** at 345 nm should excite the Py groups selectively. Subsequently cyclization will lead to intramolecular fluorescence quenching by singlet energy transfer. Because of the weak oscillator strength of the benzil absorbance between 380 and 410 nm, energy transfer should require close proximity (adjacency) between Py* and Bz.

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