after partial degradation. The small shift in molecular weight distribution is consistent with degradation initiated by head-to-head bond cleavage (Scheme I).

We do not yet know the cause for the observed rate increase during isothermal degradation of PMMA-HH with $DP_o = 46$ (Figure 4). We also observe unexpected thickness effects on the degradation of PMMA-HH samples. The degradation rate often increases as the sample thickness decreases. It is possible that main-chain head-to-head scission is more efficient near a surface than in the bulk polymer melt; however, these details will require further study.

Conclusion. We have demonstrated that incorporation of "weak" head-to-head bonds in a PMMA chain can reduce the polymer degradation temperature by promoting facile homolytic scission of the chain. However, when $DP_o > 200$, the apparent rate of main-chain scission is greatly reduced by extensive cage recombination that overwhelms the effect of head-to-head bonds.

Many proposed (accepted) polymer degradation mechanisms anticipate an initial main-chain scission in the first step. Our results suggest that main-chain scissions will be kinetically inhibited relative to side-group or chain-end cleavage. Initial cleavage of side-chain groups followed by β-scission might initiate polymer degradation when the bond dissociation energies for side-group and main-chain scissions are similar.

Future studies will address the surface-to-volume effects on PMMA-HH thermal degradation. We also plan to prepare PMMA-HH where the head-to-head bond is at the chain end. We anticipate that chain-end head-to-head bonds will not undergo as much cage recombination as internal head-to-head bonds.

Experimental Section. Experimental procedures used to monitor PMMA thermal degradation have been reported previously.[11]

PMMA-HH was prepared by group-transfer polymerization[1,2] using the difunctional initiator 1,4-bis(trimethylsiloxy)-1,4-dimethoxy-2,3-dimethylbutadiene (I). The initiator, I, is prepared by standard procedures from 2,3-dimethyl dimethylsuccinate, lithium diisopropylamine, and trimethylsilyl chloride.[13] The initiator synthesis gives three regioisomers of I (*Z*,*Z*; *E*,*E*; and *E*,*Z*), which could be separated chromatographically; however, a mixture of the three isomers was used for polymer initiation. Both the rate of polymerization (slow) and the resultant MW distributions ($M_w/M_n \sim 1.3$) indicate that the rate of initiation (k_i) is slower than the rate of propagation (k_p) for these conjugated difunctional initiators. The presence of head-to-head bonds in the polymer is dictated by the established mechanism of group-transfer polymerization.[1,2,14,15]

Acknowledgment. Edward A. Lipka, Joseph R. Butera, and J. R. Crompton, Jr., provided excellent technical assistance throughout this research.

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Received August 9, 1989;
Revised Manuscript Received October 24, 1989

Concerning the Miscibility of PVC–PVAc Blends

In the absence of specific interactions most homopolymer blends are immiscible. Accordingly, there has been a great deal of interest in the experimental observation of "miscibility windows" in mixtures of certain copolymers, even though binary blends of homopolymers of the various constituents are immiscible.[1–4] This has been explained on the basis of a "repulsive" interaction between the units of the copolymer.[2,5,6] For example, for a system containing a copolymer 1 comprised of two different monomer units, A and B, blended with a homopolymer 2 having monomer units, C, a Flory–Huggins free energy of mixing may be written as

$$\frac{\Delta G_M}{RT} = \frac{\Phi_1}{N_1}\ln \Phi_1 + \frac{\Phi_2}{N_2}\ln \Phi_2 + \Phi_1\Phi_2\chi_{\rm blend} \qquad (1)$$

where $\chi_{\rm blend}$ is given by

$$\chi_{\rm blend} = \chi_{\rm AC}\Phi_{\rm A} + \chi_{\rm BC}\Phi_{\rm B} - \chi_{\rm AB}\Phi_{\rm A}\Phi_{\rm B} \qquad (2)$$

and Φ_1 is the volume fraction of the $(A_{\Phi_A}B_{\Phi_B})_n$ copolymer, Φ_2 is the volume fraction of the homopolymer C, and N_1, and N_2 are the respective degrees of polymerization of the chains. It follows that even if $\chi_{\rm AB}$, $\chi_{\rm AC}$, and $\chi_{\rm AB}$ are all positive, $\chi_{\rm blend}$ can still be negative, depending upon the composition of the copolymer and the relativer magnitudes of the individual segmental interaction parameters.

While the above concept is elegant and appealing, one must question whether or not it has been truly tested experimentally. It is well established that the presence of specific favorable intermolecular interactions between the components of a binary polymer blend favors miscibility. In eq 2 this is equivalent to $\chi_{\rm AC}$ and/or $\chi_{\rm BC}$ assuming negative values in which case it is not necessary to invoke a "repulsion" between the different monomer units of the copolymer to obtain an overall negative $\chi_{\rm blend}$. For example, blends involving poly(vinyl chloride) (PVC), poly(vinyl acetate) (PVAc), and various copolymers that include a third comonomer have been the subject of detailed studies.[8–10] Although specific interactions involving the acetate carbonyl group have been identified,[7,8] the work of Shiomi, Karasz, and MacKnight[9] and Cruz-Ramos and Paul[10] results in the determination of a positive χ for interactions between PVC and PVAc segments. In their study of PVC–poly(ethylene-*co*-vinyl acetate) (EVA) blends Cruz-Ramos and Paul[10] reviewed the literature and

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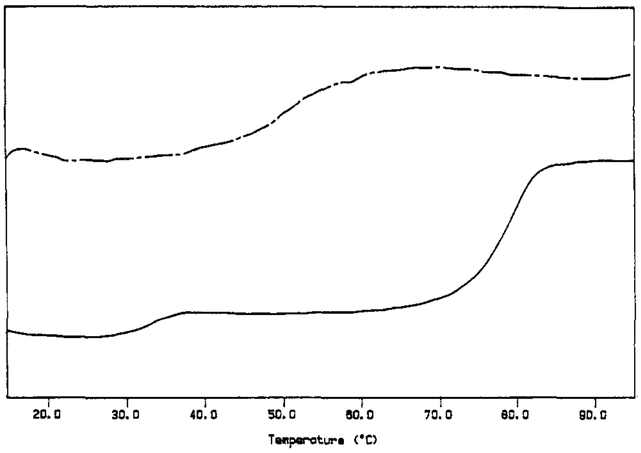

Figure 1. DSC thermograms of PVC–PVAc blends (25:75 wt %): top, cast from MEK; bottom, cast from THF.

state categorically, "The immiscibility of PVC with either PE or PVAc, which constitute the two ends of the composition plot, is a point of total agreement in these reports". Obviously, if for some reason these reports of the immiscibility of PVC–PVAc are erroneous, then the use of a binary interaction or repulsion model, particularly for blends of poly(vinyl acetate-*co*-vinyl chloride) with chlorinated poly(vinyl chloride) (CPVC),[9] would also appear inappropriate. In this short communication we will describe evidence for the miscibility of PVC–PVAc blends.

There are unfortunately many conflicting reports in the literature concerning the miscibility of PVC–EVA blends. Sample preparation, a strong $\Delta\chi$ effect,[11] relatively low lower critical solution, and degradation temperatures conspire to make the system difficult to study experimentally. Nonetheless, in a painstaking review all the available data, Cruz-Ramos and Paul[10] concluded that a wide compositional range of EVA's containing from about 45% to 87% VAc are miscible with PVC but, as we noted above, also concluded that the homopolymers are immiscible. Indeed, using PVC and PVAc polymers that have been described elsewhere,[8,12] an initial thermal analysis of blends prepared in a similar manner to that described by Shiomi, Karasz, and MacKnight[9] (as films from THF solutions) confirmed that these materials are immiscible (multiphased). Typical thermograms, as shown at the bottom of Figure 1, exhibit two distinct T_g's, corresponding to the essentially pure PVC and PVAc components. Postulating that phase separation might be induced by the THF (the so-called $\Delta\chi$ effect), we prepared films of PVC–PVAc blends as a function of varying solution concentrations, evaporation rates, film thicknesses, and preparation temperatures in an attempt to minimize possible solvent-induced phase separation, but to no avail. In all cases the films prepared from THF were obviously multiphased. Thus one is forced to the conclusion that PVC–PVAc blends are either inherently immiscible at ambient temperature or that evaporation of THF produces a very powerful $\Delta\chi$ effect. The evidence points to the latter.

PVC is not a very soluble polymer. In fact, there are few low boiling point solvents for PVC, and they are limited to organic molecules that are known to form specific favorable intermolecular interactions with the polymer (e.g. the interaction between the –CHCl– group of PVC with the ether oxygen of THF or the carbonyl group of a ketone). On the other hand, PVAc is a relatively soluble polymer and will dissolve in solvents of similar chemical structure in concert with the adage "like likes like"—largely a combinatoral entropy driven phenomenon. Accordingly, it is reasonable to assume that THF will preferentially associate with PVC in ternary mixtures of PVC/PVAc/THF when the concentration of THF reaches a critically low value—the affinity of THF for PVC being much stronger than that for PVAc. Support for this hypothesis comes from the following experiment. Films prepared in aluminum pans under conditions of very slow solvent evaporation show evidence of gross phase separation. Thermal analysis of specimens cut from the central portion of the film showed them to be significantly rich in PVC while those cut from the periphery of the film were found to be very rich in PVAc. This we explain in the following manner. The peripheral region dries before the central region of the film. At the interface between the dry and "wet" regions of the film separation is occurring into a rich PVAc phase and a PVC-rich phase containing residual THF. The latter is transported toward the center leading to the gross phase separation observed.

Finally, it follows that if we can find a common solvent (or solvent mixture) for the PVC–PVAc blends, one that does not interact so strongly with PVC, it still may be possible to prepare a single phase material. As mentioned above, the choices are very limited since we require a low boiling solvent that can be removed from the film at temperatures below the onset of degradation (<120 °C). Fortunately, methyl ethyl ketone (MEK) turns out to be such a solvent. Films of PVC–PVAc blends of varying compositions were prepared from MEK solutions. Evaporation of the solvent was performed slowly over a period of 3 days in a closed petre dish at room temperature. The samples were then heated to 70 °C for 1 day under vacuum to remove any residual solvent. The thermograms recorded from PVC–PVAc blend films cast from MEK displayed only one, relatively broad, intermediate T_g, as illustrated at the top of Figure 1. This is good evidence that a miscible system has been formed.

If PVC–PVAc systems are indeed miscible, is there a reasonable alternative interpretation of the observed phase behavior of blends involving PVC? We believe there is. Because strong interactions between different molecules are often localized in specific functional groups, we have employed a model where the free energy of mixing can be described by the equation[13]

$$\frac{\Delta G^{\mathrm{M}}}{RT} = \frac{\Phi_{\mathrm{A}}}{N_{\mathrm{A}}} \ln \Phi_{\mathrm{A}} + \frac{\Phi_{\mathrm{B}}}{N_{\mathrm{B}}} \ln \Phi_{\mathrm{B}} + \Phi_{\mathrm{A}}\Phi_{\mathrm{B}}\chi + \frac{\Delta G_{\mathrm{H}}}{RT} \qquad (3)$$

Φ_A and Φ_B and N_A and N_B are the volume fractions and degrees of polymerization of polymers A and B, respectively, and χ is the polymer–polymer interaction parameter. This is the Flory–Huggins relationship, but with an added term, $\Delta G_H/RT$, to account for the presence of favorable intermolecular interactions. In the systems we have studied these are usually hydrogen bonds, but any strong localized interaction that results in the formation of associated species can be described in such terms. Although it appears that we have simply added a term to account for strong interactions, we have recently been able to formally obtain this result using a Flory lattice model.[14] This will be considered elsewhere. The crucial point we wish to make here, and one that transcends the consideration of the validity of the association models we have been using, is that if there is a favorable interaction between components of a blend, miscibility will ultimately depend upon the balance between the number and strength of such favorable interactions, which we include in a $\Delta G_H/RT$ term, and unfavorable dispersive interactions, which we describe by a conventional χ parameter. Following Scott,[15] we determine an average χ for blends

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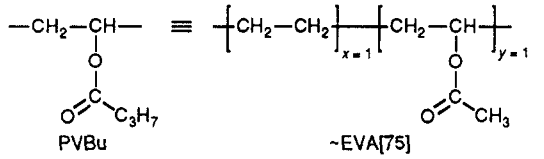
involving copolymers and herein lies a major conceptual difference between our approach and that of groups advocating the use of repulsion models for copolymer blends. We make no distinction between, for example, PVC blends with the "homopolymer" poly(vinyl *n*-butyrate) (PVBu) and its isomorphous equivalent, an average repeat of an equimolar EVA "copolymer".



It could be argued that PVBu is a "copolymer" and an appropriate χ can be defined between the CH_2's in the side chain and the residual vinyl acetate unit. But instead of separating just the ethylene group in this manner, why not include the methyl and the main chain–CH_2–CH–groups? Where does one draw the line? Taking this process to the extreme, nearly all polymers can be considered "copolymers" (the only exceptions being polymethylene, polytetrafluoroethylene, and the like, and even these polymers can be reduced to different atomic contributions). For most miscible blends there is usually evidence for some favorable interaction, and we believe it is better to attempt to separate these from the unfavorable interactions embodied in an average nonassociated solubility parameter.

The miscibility behavior of PVC blends with EVA copolymers now follows in a straightforward manner. The homopolymers PVC and PVAc are miscible, but as the concentration of ethylene units in the EVA copolymer (or alternatively, in the homologous series of the homopolymers PVAc, PVPr, PVBu, etc.) is raised, the number of favorable interactions decreases. χ also changes, and at some critical concentration of ethylene units the homopolymer–copolymer blend becomes immiscible. In the more complex case of the poly(vinyl acetate-*co*-vinyl chloride) blends the polymer molecules strongly self-associate, and this must be balanced with the competing interactions that would form with CPVC. Furthermore, given the results presented here we would also anticipate strong $\Delta\chi$ affects in PVAc–CPVC blends.

Finally, it is important to note that specific interactions should be described by a free energy term, so that it is possible to have a positive enthalpy of mixing (as Cruz-Ramos and Paul[10] determined for PVC–PVAc model compounds), providing that this is compensated by a gain in entropy upon mixing. This is common in, for example, hydrogen-bonded systems where one of the components self-associates. As a result, more hydrogen bonds between like molecules can be broken upon mixing than are formed between unlike molecules. This can result in a large positive enthalpy of mixing that is more than compensated by a gain in "freedom" or entropy of the no longer associated molecules or segments.

Conclusions. 1. Under the appropriate experimental conditions a miscible blend of PVC and PVAc can be prepared from a solution of the polymers in MEK at room temperature.

2. PVC–PVAc blend samples prepared from THF solution were found to be grossly phase separated that apparently arises from a powerful $\Delta\chi$ effect.

3. PVC–EVA blends has been previously considered to represent one of the classic examples of a special class of blends where a homopolymer (PVC) is miscible with a range of copolymers of specific composition (EVA) but immiscible with both homopolymers (PE and PVAc) derived from the monomers used to synthesize the copolymer. The results presented here cast doubt on this assertion.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation, Polymers Program, the Shell Foundation, and ARCO Chemical Co.

Registry No. PVC, 9002-86-2; PVAc, 9003-20-7.

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Received August 8, 1989;
Revised Manuscript Received September 25, 1989

Screening Effect on Viscoelasticity near the Gel Point

There has recently been many experimental investigations[1-14] of the static and dynamic properties of branched polymers near the gel point. The chief objective of these studies is to verify the theories of gelation and properties of polymers in the vicinity of the sol–gel transition. There are two theories of gelation. One is the classical theory of Flory,[15,16] Stockmayer,[17] and Zimm.[18] The other is the percolation theory.[19,20] Many researchers[1-10] have demonstrated clearly that the percolation theory is quite successful in predicting the static properties of branched polymers (such as distributions of size and mass of clusters, correlation length, and fractal dimension) near the gel point. However, the status is not so clear regarding the dynamical properties of branched polymers near the gelation threshold.

In a typical experiment, difunctional polymers or monomers are mixed with tri- or tetrafunctional molecules (cross-linking agents or star polymers) under suitable chemical conditions, and the cross-linking process is carried out for a certain duration. The extent of cross-linking is controlled by either "poisoning" the reaction at a known time of reaction or controlling the stoichiometry and running the reaction to completion. The samples obtained at different extents of the cross-linking reaction are then

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