deuteriated solvent. Elemental analysis failed to detect any carbon or sulfur in the polymer. Moreover, all the $NPCl_2$ units in the system were accounted for by the quantitative recovery of cyclic oligomers and polymer. Thus, carbon disulfide appears to be unreactive toward chlorophosphazenes over the 25–250 °C temperature range.

Influence of Polymerization Time. At 250 °C, in 4.75 mol/L solution in carbon disulfide, the conversion of $(NPCl_2)_3$ to $(NPCl_2)_n$ increased from 20% at 10 h to 70% after 144 h. The polymer was un-cross-linked and had a GPC molecular weight near 7×10^5. During the same time period, the yield of higher cyclic species (tetramer through octamer) increased from 2.5 to 11.4%.[13] The polymer molecular weights appeared to be independent of polymerization time at a given concentration but to decrease as the concentration of $(NPCl_2)_3$ in carbon disulfide was lowered.

Source of Higher Cyclic Oligomers. The formation of the cyclic oligomers, $(NPCl_2)_{4-8}$, in the polymerization system is of some mechanistic interest. Preliminary data have been obtained that these higher oligomers are not present during the initial stages of the reaction but that their concentration rises as the amount of high polymer increases. Moreover, solutions of pure $(NPCl_2)_n$ in carbon disulfide yielded mixtures of $(NPCl_2)_{4-8}$ after several days at 250 °C. Thus, we conclude that ring–ring equilibration to yield $(NPCl_2)_{4-8}$ directly from $(NPCl_2)_3$ is probably not a significant source of these products.[14] Instead, thermal depolymerization of $(NPCl_2)_n$ to a mixture of cyclic oligomers may be the main oligomerization pathway.

Acknowledgment. This work was supported by the Public Health Service through the National Heart, Lung and Blood Institute, Grant No. 5 R01 HL11418.

Registry No. 1, 25231-98-5; 2, 26085-02-9; CS_2, 75-15-0.

References and Notes

(1) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.

(2) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.

(3) Allcock, H. R. *Phosphorus–Nitrogen Compounds*; Academic: New York, 1972.

(4) Patat, F.; Kollinsky, F. *Makromol. Chem.* **1951**, *6*, 292.

(5) Konecny, J. O.; Douglas, C. M.; Gray, M. Y. *J. Polym. Sci.* **1960**, *42*, 383.

(6) Konecny, J. O.; Douglas, C. M. *J. Polym. Sci.* **1959**, *36*, 195.

(7) MacCallum, J. R.; Tanner, J. *J. Polym. Sci., Part B* **1969**, 743.

(8) Kajiwara, M.; Saito, H. *Kogyo Kagaku Zasshi* **1963**, *66*, 621.

(9) Kajiwara, M.; Saito, H. *Kogyo Kagaku Zasshi* **1964**, *67*, 1002.

(10) Fieldhouse, J. W.; Graves, D. F. *Proc. Int. Nat. Conf. Phosphorus Chem. 1981. ACS Symp. Ser.* **1981**, *No. 171*, 315.

(11) Caglioti, V.; Cordischi, D.; Mele, A. *Nature (London)* **1962**, 195, 491.

(12) Kajiwara, M.; Shiomoto, K. *Polymer* **1984**, *25*, 93.

(13) The following percentage yields were obtained for polymer and (in parentheses) total $(NPCl)_2)_{4-8}$: 0 h, 0% (0%); 10 h, 20% (2.5%); 24 h, 30% (2.7%); 41 h, 40% (6.3%); 75 h, 60% (7.2%); 144 h, 70% (11.4%).

(14) Unless $(NPCl_2)_3$ is capable of fragmentation to monomer and linear dimer, it would be difficult to explain the direct formation of $(NPCl_2)_4$ and $(NPCl_2)_5$.

Dependence of T_g on Composition for a Compatible Polymer/Oligomer Blend

PETER B. RIM* and E. BRUCE ORLER

Louis Laboratory, S. C. Johnson & Son, Inc., Racine, Wisconsin 53403. *Received June 10, 1986*

Compatible polymer blends have been studied extensively in the past decade.[1,2] One of the goals of this research is to develop materials whose properties can be tailored by varying the ratios of the properly chosen blend components. It can be envisioned that alloys with novel properties somewhat intermediate between the properties of the blend constituents can be developed with minimum expense by utilization of existing polymers.

A relatively rapid way to determine the level of miscibility for mixtures of macromolecules is differential scanning calorimetry (DSC). The presence of a single blend glass transition temperature (T_g), intermediate to the T_g's of the individual components, is the criterion used to define compatibility by this method.[1] A variety of relationships that predict the compositional dependence of T_g for blends and copolymers have been discussed.[3-9] Development of such an equation is important for theoretical reasons and because of the large influence of T_g on macroscopic properties. Couchman[3-5] has derived such a relationship based on entropic considerations:

$$\ln T_g = \frac{x_1 k \ln T_{g_1} + x_2 \ln T_{g_2}}{x_1 k + x_2} \tag{1}$$

where subscripts 1 and 2 correspond to the blend components, x is the weight fraction of the blend component, $k = \Delta C_{p_1}/\Delta C_{p_2}$, and ΔC_p is the difference in heat capacity below and above the pure component T_g's. It has been mentioned by Couchman[3] that if $T_{g_1} \approx T_{g_2}$ eq 1 yields

$$T_g = \frac{x_1 k T_{g_1} + x_2 T_{g_2}}{x_1 k + x_2} \tag{2}$$

For the purpose of later discussion we note that if $k = \Delta\alpha_1/\Delta\alpha_2$, where $\Delta\alpha$ is the difference in volume expansion coefficient below and above T_g, eq 2 is identical with the Gordon–Taylor expression.[9] It has also been pointed out[3] that if $\Delta C_{p_1} T_{g_1} \approx \Delta C_{p_2} T_{g_2}$ eq 2 results in the Fox relationship[7] (eq 3) and if $\Delta C_{p_1} \approx \Delta C_{p_2}$ eq 1 simplifies to the empirical equation of Pochan[6] (eq 4):

$$\frac{1}{T_g} = \frac{x_1}{T_{g_1}} + \frac{x_2}{T_{g_2}} \tag{3}$$

$$\ln T_g = x_1 \ln T_{g_1} + x_2 \ln T_{g_2} \tag{4}$$

Poly(vinyl chloride) (PVC) has been shown to be compatible or semicompatible with a variety of other macromolecules.[10-24] In a number of instances the Fox equation has provided a good fit to the experimentally determined glass transition temperatures of these blends.[19-22] This may have occurred because the approximations necessary to yield this equation were met. For example, the product of ΔC_p and T_g is believed to be a constant for several polymers.[25] The materials of interest in this investigation, PVC and a styrenic oligomer, will be shown to be thermodynamically miscible. This system offers the opportunity to test the validity of Couchman's equation since it will be shown that for these materials $\Delta C_{p_1} \neq \Delta C_{p_2}$ and $\Delta C_{p_1} T_{g_1} \neq \Delta C_{p_2} T_{g_2}$.

Experimental Section

The blend components used in this study are PVC and an oligomer composed of (w/w) 34% α-methylstyrene, 28% styrene, 25% acrylic acid, and 13% carbitol ester of acrylic acid. The oligomer was provided by J. Allaway of S. C. Johnson & Son, Inc., and the PVC is a stabilized extrusion-grade material provided by Vista Chemical Co. Molecular weights relative to polystyrene standards in tetrahydrofuran were determined via gel permeation chromatography (GPC) by C. Weiss of S. C. Johnson & Son, Inc. (Table I). C. Beatty of the University of Florida prepared the blends by a melt-extrusion process at 160–200 °C. After blending, representative samples were analyzed by GPC to ensure that cross-linking or chain scission had not occurred. Differential

0024-9297/87/2220-0433$01.50/0 © 1987 American Chemical Society

Table I

component	M_n	M_w	T_g, K	$C_p < T_g$[a]	$C_p > T_g$[a]	ΔC_p[a]	$\Delta C_p T_g$
PVC	68200	164000	354	1.04	1.31	0.27	95.6
oligomer	1070	3320	281	1.14	1.61	0.47	132.1

[a] J/(g °C).

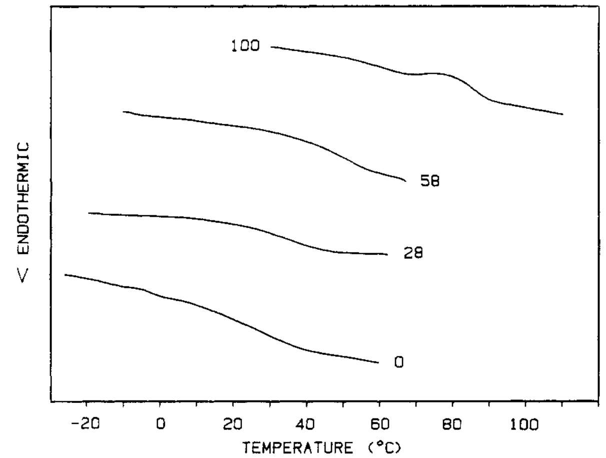

Figure 1. Representative DSC traces of the pure blend components and blends. The curve designations correspond to percent PVC.

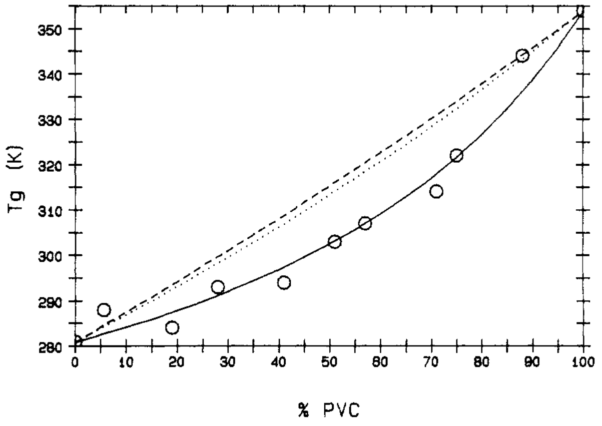

Figure 2. Plot of T_g vs. blend composition depicting experimental data and theoretical relationships: (O) experimental data; (---) Pochan equation; (···) Fox equation; (—) Couchman equation.

scanning calorimetry (DSC) was performed on a Du Pont 910 DSC/9900 thermal analyzer at a heating rate of 20 °C/min. Temperature calibration was accomplished by using indium and high-purity water. T_g's are defined as the onset of the transition (i.e., the intersection point of the pre-T_g base line and a line drawn tangent to the slope of the change in heat capacity associated with T_g). The heat capacities immediately below and above the T_g's of the pure components were determined by the usual method[26,27] and are summarized in Table I.

Results and Discussion

Figure 1 depicts representative DSC traces of the pure blend components and blends, and Figure 2 summarizes the DSC-derived T_g's as a function of composition. For the compositions studied, the DSC behavior indicates that this system is compatible because a single composition-dependent T_g is observed for the blends. Although it is not clear whether the driving force for this miscibility is entropic or enthalpic in nature, it is realized that if only one component in a mixture is of low molecular weight, a considerable entropy of mixing still exists.[28] Also plotted in Figure 2 are curves based on the equations of Fox, Pochan, and Couchman. The equations of Fox and Pochan, which require only the T_g's and weight fractions of the pure components, do not provide a reasonable fit to the data. We believe that this occurs because the assumptions relevant to the derivation of these relationships, mainly $\Delta C_{p_1} \approx \Delta C_{p_2}$ and $\Delta C_{p_1} T_{g_1} \approx \Delta C_{p_2} T_{g_2}$, are not met (Table I).

The remaining curve on the graph, which fits the experimental data well, results from fitting Couchman's original expression (eq 1) to the data by varying the parameter k and employing the experimentally determined pure component T_g's. The resulting "best fit" k value of 0.47 is in fair agreement with the experimentally derived k value of 0.57 which was calculated from the heat capacity data in Table I ($k = \Delta C_{p_1}/\Delta C_{p_2}$). It is noted that if eq 2 is fit to the experimental data, a curve that mimics the Couchman fit is developed for a k value of 0.42. For this case, k corresponds to $\Delta\alpha_1/\Delta\alpha_2$ in terms of the Gordon–Taylor expression. Since values of $\Delta\alpha$ are not available, it is impossible to compare the k value of 0.42 to an experimentally determined value.

Recently, Goldstein[29] has criticized the derivation of the thermodynamically based Couchman equation. He argues that an assumption of Couchman's approach, mainly that the entropy of mixing at T_g is continuous, will not in general be satisfied. Perhaps this is the reason for the imperfect agreement between the experimental k value and the "best fit" k value. Finally, Couchman's relationship has been shown to fail for systems with strong enthalpic interactions and should not be employed for these specific cases.[30]

Conclusion

It has been shown that when there are significant differences in ΔC_p and/or $\Delta C_p T_g$ between blend components it is better to use Couchman's relationship than the Fox or similar equations when estimating blend T_g's. DSC can be readily used to determine both pure component parameters, ΔC_p and T_g, necessary to perform this analysis.

Registry No. PVC, 9002-86-2; (α-methylstyrene)(styrene)(acrylic acid)(carbityl acrylate) (copolymer), 105336-87-6.

References and Notes

(1) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer–Polymer Miscibility*; Academic: New York, 1979.
(2) Paul, D. R.; Newman, S. *Polymer Blends*; Academic: New York, 1978; Vols. 1 and 2.
(3) Couchman, P. R. *Phys. Lett. A* **1979**, *70*, 155.
(4) Couchman, P. R. *Macromolecules* **1978**, *11*, 1156.
(5) Couchman, P. R. *Macromolecules* **1980**, *13*, 1272.
(6) Pochan, J. M.; Beatty, C. L.; Pochan, D. F. *Polymer* **1979**, *20*, 879.
(7) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.
(8) Wood, L. A. *J. Polym. Sci.* **1958**, *28*, 319.
(9) Gordon, M.; Taylor, J. S. *J. Appl. Chem.* **1952**, *2*, 493.
(10) Ziska, J. J.; Barlow, J. W.; Paul, D. R. *Polymer* **1981**, *22*, 918.
(11) Walsh, D. J.; McKeown, J. G. *Polymer* **1980**, *21*, 1330.
(12) Malik, T. M.; Prud'homme, R. E. *Macromolecules* **1983**, *16*, 311.
(13) Garton, A.; Aubin, M.; Prud'homme, R. E. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 45.
(14) Hubbell, D. S.; Cooper, S. L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1143.
(15) Prud'homme, R. E. *Polym. Eng. Sci.* **1982**, *22*, 90.
(16) Bandyopadhyay, P. K.; Shaw, M. T. *J. Appl. Polym. Sci.* **1982**, *27*, 4323.
(17) Wang, C. B.; Cooper, S. L. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 11.
(18) Varnell, D. F.; Runt, J. P.; Coleman, M. M. *Polymer* **1983**, *24*, 37.

(19) Aubin, M.; Prud'homme, R. E. *Macromolecules* **1980,** *13,* 365.
(20) Koleske, J. V.; Lundberg, R. D. *J. Polym. Sci., Part A-2* **1969,** *7,* 795.
(21) Zakrzewski, G. A. *Polymer* **1973,** *14,* 347.
(22) Kondo, T.; Kitayama, M.; Vogl, O. *Polym. Bull. (Berlin)* **1982,** *8,* 9.
(23) Lehr, M. H. *Polym. Eng. Sci.* **1985,** *25,* 1056.
(24) Vorenkamp, E. J.; ten Brinke, G.; Meijer, J. G.; Jager, H.; Challa, G. *Polymer* **1985,** *26,* 1725.
(25) Boyer, R. F. *J. Macromol. Sci., Phys.* **1973,** *7,* 487.
(26) Eysel, W.; Breuer, K. H. *Techscan* **1982,** 2.
(27) E. I. du Pont de Nemours and Company, *910 DSC Operator's Manual,* 1983.
(28) Patterson, D. *Polym. Eng. Sci.* **1982,** *22,* 64.
(29) Goldstein, M. *Macromolecules* **1985,** *18,* 277.
(30) Rodriguez-Parada, J. M.; Percec, V. *Macromolecules* **1986,** *19,* 55.

Nitroxide Spin Label Dimer Pairing: A Cautionary Note

ROBERT G. KOOSER

Knox College, Galesburg, Illinois 61401.

Received August 12, 1986

The spin label technique has been widely used to study the dynamics of polymers in both the solution and the solid state and has been reviewed several times.[1-3] Although the technique has wide applicability, it appears that with certain types of spin labels a dimerization can take place which can obscure the interpretation of the results.

During an investigation of the polymer dynamics of nitroxide-labeled poly(hexene sulfone) (PHS) in dilute solutions, we encountered what appeared to be superposition electron spin resonance (ESR) spectra (see Figure 1), which are usually attributed to spin labels existing in two different motional domains. A careful examination of these spectra convinced us that the conventional interpretation in this case was incorrect and that the broader spectrum arises from dimer formation between two nearby nitroxide labels. An examination of the recent literature shows that dimer spectra may have occurred in other systems.

The self-association of free nitroxide radicals even in fairly dilute solutions has been known for some time, but evidently this phenomenon has not been widely appreciated. Marshall[4] reported the association of 2,2,5,5-tetramethyl-3-carboxypyrrolidine oxyl (carboxy–TEMPYO) and measured the exchange energy, equilibrium constants, and ΔH's. Later Veloso and Rassat[5] determined dipolar splittings and concentration dependences of dimer ESR spectra for two TEMPYO species, 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), 2,2,7,7-tetramethylhexahydro-1,4-diazepin-5-one 1-oxyl, and 2,2,5,5-tetramethyloxazolidine 1-oxyl. The Veloso and Rassat article[5] clearly demonstrates that the association can occur at concentration levels usually thought to be dilute enough to avoid serious radical–radical interactions. They report that dimer spectral lines for carboxy-TEMPYO and its methyl ester appear at concentrations as low as 1.1×10^{-4} M. In the case of TEMPO and the oxazolidine 1-oxyl, both commonly used as labels, the minimum concentration was found to be 5×10^{-3} M, a concentration too high for most label studies. Clearly, in the case of the use of TEMPYO labels, one must be careful in data interpretation.

The confusion comes about because of a similarity in superposition spectra and dimer spectra under certain conditions. The theory of the ESR spectral appearance of radical dimers is the same as the well-known theory for biradicals.[6] When the exchange energy is less than the hyperfine coupling constant, the dimer spectrum has the typical nitroxide three lines separated by the coupling constant, a_N, but with sidebands from weakly allowed transitions.[5-7] Thus the spectrum takes on the appearance of the superposition of mobile and immobile labels.

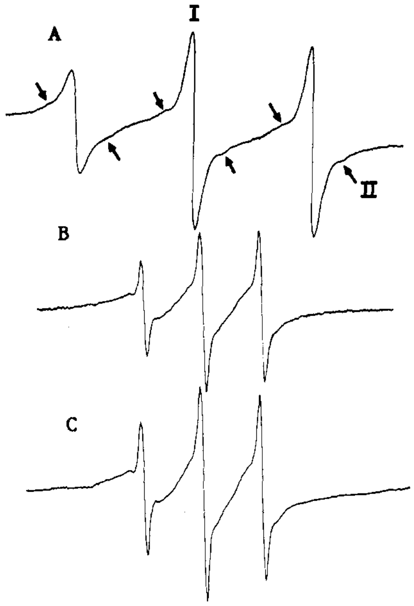

Figure 1. ESR spectra of TEMPYO-labeled poly(hexene sulfone) in toluene solution as a function of temperature (A, 22 °C; B, 12 °C; C, −28 °C) showing the "normal" three-line nitroxide spectrum (I) and the sidebands (II, marked by arrows) arising from radical pairing.

In our case, we synthesized a 1-hexene:1-hexen-6-ol (3–5 mol % alcohol) polysulfone by free radical initiated copolymerization of SO_2 and olefins at −10 °C in open tubes. The polymer was labeled by reaction of the copolymer with the acid chloride of carboxy-TEMPYO in dry benzene with excess dry pyridine. Spin label studies were done in dry, degassed toluene solution at 1.5 wt % polymer concentrations using a Varian V-4500 EPR spectrometer to record the EPR spectra. Spin concentration measurements using a dual sample cavity[8] indicated that the labeling was complete (3.0 mol % calculated; 3.5 ± 0.5 mol % measured). Figure 1 shows sample spectra as a function of temperature. The spectra resemble those obtained from the label in two different motional domains, a tantalizing interpretation considering the partial helical configuration[9,10] of this polymer. For convenience, let I designate the three sharp lines of the spectrum and II designate the broader, less intense sidebands.

Attributing the two portions to two different motional domains becomes unlikely in light of experimental evidence. Comparisons of ESR spectra of the labeled PHS in toluene, CH_2Cl_2, dioxane, and acetone-d_6 demonstrate no appreciable solvent dependence to the intensity ratios of I to II. This would be a surprising result if I and II resulted from motional differences as dielectric relaxation data show marked solvent dependence for PHS in benzene and dioxane.[11] The evidence points to an intramolecular process (association of labels in the same polymer molecule) where we note that the solutions are at the equivalent of 5×10^{-3} M, far above the minimum concentration for observable dimer effects for TEMPYO-type labels.[5] The ESR spectra of 0.15 wt % labeled PHS in toluene show no reduction in the intensity of II compared to I, further confirming the intramolecular origin.

Additional evidence is indicated by the ESR spectrum of labeled, nonhelical[9] poly(cyclohexene sulfone) (PCHS) using 3 mol % 1-hexen-6-ol at a density of 17% of the

0024-9297/87/2220-0435$01.50/0