Figure 2 Logarithm of the specific absorbancy (log e_i) as a function of degradation time. (K = 69, 180°C, Ar; (———), gel point)

different PVC samples. In all cases essentially the same results were obtained by the different methods.

According to our experience, gel point values of the same reliability, as found by the gravimetric or viscometric method can be obtained by the photometric determination more quickly and with less effort.

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Electron spin resonance studies of spin-labelled polymers: 15. Spin probe measurements of plasticized poly(vinyl acetate)

A. T. Bullock, G. G. Cameron, C. B. Howard and N. K. Reddy
Department of Chemistry, University of Aberdeen, Old Aberdeen, Scotland AB9 2UE, UK
(Received 10 October 1977)

INTRODUCTION

The glass transition temperature, T_g, of an amorphous polymer is often associated with the β relaxation of mechanical and dielectric loss measurements. The transition is thus associated with the onset of main chain segmental motion and the result of any measurement of T_g will depend on the characteristic time of the experiment.

The spin probe technique is the most recent addition to methods for studying relaxations in amorphous polymers. The experiment involves the preparation of a dilute dispersion of a stable nitroxide radical in the relevant polymer and a study of the changes in shape of the electron spin resonance spectrum as a function of temperature. At low temperatures, the spectrum is dominated by the anisotropic coupling between the unpaired electron and the ^{14}N nucleus. Subtle changes in shape of the dispersion mode under varying conditions of microwave power and field modulation frequency enable correlation times τ as long as 10^{-5} sec to be mea-sured[1]. In the region $10^{-9} < \tau < 10^{-7}$ sec there are well defined changes in the absorption mode, in particular the separation between the high- and low-field extrema decreases monotonically with τ^{2-4}. It is expected that a marked change in shape will occur when

$$\tau^{-1} \sim \frac{4\pi}{3} \left[T_{zz} - \frac{1}{2} (T_{xx} + T_{yy}) \right]$$

where the T's are the principal values of the hyperfine coupling tensor. Typical values for T_{xx}, T_{yy} and T_{zz} for dialkyl and saturated cyclic nitroxides lead to values for τ at this critical region of $\sim 3 \times 10^{-9}$ sec. For longer correlation times, the spectral shape is characteristic of the solid whilst at shorter times the typical motionally-narrowed spectrum is observed.

Following the early work of Rabold[5], Kumler and Boyer have made extensive use of an empirical parameter T_{50G} to characterize this transition region. This is the temperature at which the extrema separation is 50 gauss and a correlation has been established between T_g and T_{50G} for nineteen different polymers and co-polymers using 2,2',6,6'-tetramethyl-4-hydroxypiperidin-1-oxyl benzoate as the paramagnetic probe[6]. Later work by these authors has included studies of the effect of probe size[7] and an investigation of the glass transition temperatures of some block copolymers[8].

Copolymers may be conveniently considered as polymer—diluent systems. Another important class of diluents are plasticizers and the purpose of this Note is to present a correlation between T_{50G} and the weight percentage of the polymer poly(vinyl acetate) (PVAc) plasticized with dimethyl- and diethylphthalates (DMP and DEP respectively).

EXPERIMENTAL

The probe used was 2,2',5,5'-tetramethyl-3-oxazolidinyloxy (TMOZ) (I, $R^1 = R^2 = CH_3$) and was prepared from acetone and 2-amino-2-methyl-propan-1-ol using the Keana synthesis[9,10].

(I)
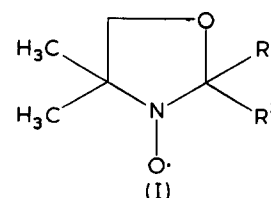
The choice of probe was governed by the consideration that in future studies using higher dialkylphthalates it would be easy to modify the synthesis so that the probe size and structure would be similar to that of the plasticizer. The PVAc was the IUPAC standard sample, kindly provided by Dr W. A. J. Bryce, and the plasticizers (BDH Ltd) were used as supplied. Samples were made up by weighing appropriate quantities of polymer and dilute solutions of the probe in the plasticizers. Mixing was mechanical. Homogeneous materials were obtained in all cases as shown by the fact that all runs were performed using heating and cooling cycles. At the highest temperatures used, homogeneous liquids were obtained and it was found that measurements of the spectral extrema were completely reversible with respect to temperature changes.

Spectra were obtained using a Varian E–109 spectrometer equipped with an E–257 variable temperature accessory. Temperatures were monitored using a Comark 3000 digital thermometer.

RESULTS AND DISCUSSION

Figure 1 shows a typical plot of extrema separation *versus* temperature. The regions of 'slow' rotation, motional narrowing and of the transition are clearly delineated. Free volume considerations[11] lead to an equation for T_g of a polymer–diluent system such that[12]:

$$\frac{1}{T_g} = \frac{1}{(w_1 + Rw_2)} \left[\frac{w_1}{T_{g1}} + \frac{Rw_2}{T_{g2}} \right] (1)$$
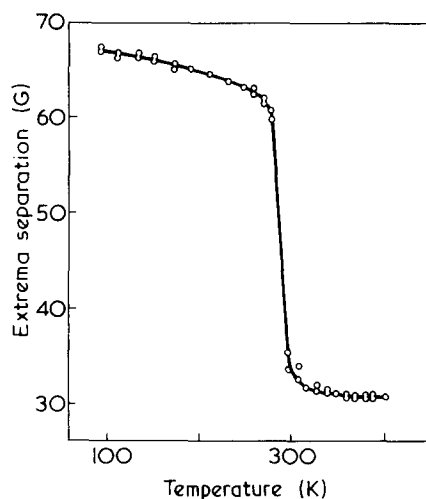

Figure 1 Extrema separation *versus* temperature for TMOZ in poly(vinyl acetate) plasticized with 20.5% diethylphthalate

where T_g is the observed glass transition temperature, the w's represent weight fractions and the subscripts 1 and 2 refer (in the present context) to the polymer and plasticizer, respectively. R is a constant which is close to unity and equation (1) may thus be written:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (2)$$

If T_{50G} correlates closely with T_g then a similar equation should hold. Rearranging equation (2) and replacing $T_{g1,2}$ with the appropriate T_{50G} yields:

$$\frac{1}{T_{50G}} = \frac{w_1(T_{50G2} - T_{50G1})}{T_{50G2} T_{50G1}} + \frac{1}{T_{50G2}} \qquad (3)$$

Figures 2 and *3* show plots of this function for PVAc plasticized with DMP and DEP, respectively. It is clear that T_{50G} for these particular polymer–diluent systems follows equation (3) closely. In particular it should be noted that T_{50G} is quite close to T_g for the pure polymer. Thus $T_{50G} = 311 \pm 1.5$K whilst $T_g = 305$K[13]. This is in marked contrast to many other probe–polymer systems where T_{50G} considerably exceeds T_g, in one case by as much as 86K[6]. These apparently disparate results may, however, be reconciled using the theory of Kusumoto *et al.*[14]. These authors used a theory due to Bueche[15] to obtain a relationship between T_{50G} and T_g in terms of f, the molar volume ratio of the probe to the polymer segment undergoing local motion at T_g. The result obtained is given in equation (4), viz.

$$T_{50G} - T_g = 52[2.9f(\ln 1/f + 1)$$
$$- 1] \qquad (4)$$

From the intercepts at $w_1 = 1$ in *Figures 2* and *3* together with the literature value[13] for T_g (305K) we obtain a value of $f = V_p/V_m = 0.125 \pm 0.005$, where V_p is the molar volume of the probe and V_m that of the mobile polymer segments. In other words, the segment volume is approximately 8 times that of the probe, which seems a wholly reasonable result.

We conclude that spin probes are a potentially useful technique in the study of polymer–plasticizer systems but further investigations of the dependence of f on various probe sizes
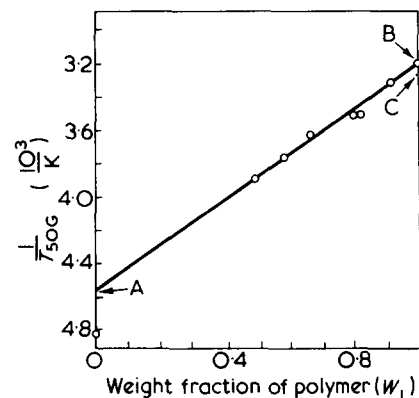

Figure 2 A plot of $10^3/T_{50G}$ *versus* the weight fraction of poly(vinyl acetate) plasticized with varying amounts of dimethylphthalate. A, 219K; B, 312.5K; C, T_g
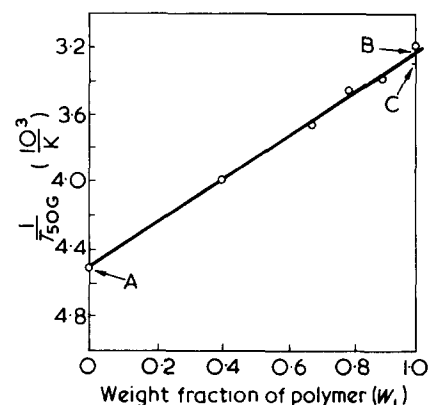

Figure 3 As *Figure 2*, but with diethylphthalate as the plasticizer. A, 222K; B, 309.6K; C, T_g

in a series of well-characterized polymers are clearly necessary.

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Synthesis and reactions of polymers with photoactive terminal groups: 2. New azo-initiator for the synthesis of polymers with N-acyldibenz[b,f] azepine terminal units

C. H. Bamford, A. Ledwith and Y. Yagci

*Department of Inorganic, Physical and Industrial Chemistry, The University of Liverpool,
Liverpool L69 3BX, UK*
(Received 1 November 1977)

INTRODUCTION

Photochemically-induced cyclodimeri-
zation[1] of ethylenically unsaturated
molecules is a well known process which
finds application in photoresist techno-
logy[2]. The reaction may be represented
generally as in equation (1) and commer-
cially important examples utilize poly-
mers having pendent or main-chain
unsaturation of the cinnamate
(ArCH=CHCOOR) or chalcone
(ArCH=CHCOR) types.

Recently it was shown[3] that N-acyl
derivatives of the dibenz[b,f]azepine
(iminostilbene) ring system (I) may be
photochemically cyclodimerized [equa-
tion (2)] with the aid of a variety of
sensitizers having triplet state energies
ranging from benzophenone (69.5 kcal/
mol) to benzil (53.7 kcal/mol). A
range of derivatives (e.g. Ib) have been
synthesized and shown to be capable
of homopolymerization or copolymeri-
zation to products which are then
photocrosslinkable via the dibenzaze-
pine substituents[4].

Attachement of structurally related
dibenzazepine derivatives to polymer
chains as terminal units would afford a
convenient procedure for chain exten-
sion or block polymer formation by
similar photoinduced cyclodimeriza-
tions. Such incorporation of specific
groups at the ends of polymer chains
may be readily accomplished by utiliz-
ing appropriately substituted initiator
molecules, especially in the case of free
radical polymerizations in which trans-

fer processes may be minimized. Photo-
sensitization by metal carbonyls, of
which there are numerous examples,
provides a convenient initiation process
for such purposes. Many initiating sys-
tems of this type include a reactive
organic halide (RX) which undergoes a
redox reaction with species resulting
from photoexcitation of the metal
carbonyl to yield a radical (R·) and a
halide anion which becomes associated
with the oxidized form of the metal as
a ligand (equation 3)[5].

Recently we have shown[6] that man-
ganese carbonyl in conjunction with
N-bromoacetyldibenz[b,f]azepine (Ic)
affords a highly convenient photo-
chemical initiating system, complying
with the well established kinetic pat-
tern[5], and yielding chain-ended func-
tionalized polymers as indicated in
equation (4).

Whether or not the product polymer
possesses one or two photochemically
active end-groups depends mainly on
the ratios of disproportionation to com-
bination for the particular polymeriza-
tion; in either case photosensitized
chain extension may be accomplished
essentially as indicated in equation (2)
with R representing a preformed poly-

(I) (a) R=CH₃; (b) R=CH=CH₂; (c) R=CH₂Br;