molten salts are much more amorphous than their pure salt counterparts. The changes approximate to 50% reduction in crystallinity. This change in crystallinity could, according to Schultz[13] be due to cross-linking in the melt phase. Such cross-linking results in the melts becoming elastic and produces a reduction in crystallinity due to increased difficulty in chain orientation.

## Conclusion

The groups IIA and IIB divalent metal dicarboxylates were obtained generally as highly viscous polymerlike materials in the molten state due to the ionic character of the metal ions. The polymeric behavior exhibited by these molten ionic metal dicarboxylates can be said to be a result of somewhat vague, dynamically shifting, unsatisfied associations first through the dicarboxylic acid chain and then between the metal dicarboxylate groups of neighboring chains. This type of association has, however, been shown to take place if the ionic character of the M–O bond of the cation is high enough. Molten lead (ionic character = 51%) dicarboxylates did not show any polymeric behavior.

The melts were thermoplastic when cooled from the melt and exhibited a relative degree of crystallinity almost as low as 50% of their pure (i.e., not melted) salt counterparts. The failure of the Mg, Ca, and Ba salts to crystallize after melting is a result of their greater tendency to form the three-dimensional network structures in the melt while the Zn and Cd salts tend to retain more linear structures which are able to partially recrystallize. In general the molten salts are characterized by high thermal stabilities ranging from 300 to 500 °C, which is a reflection of the highly ionic nature of these groups of materials. Except for lead, the molten salts which exhibit some hot-melt adhesive properties were spun into fibers which are weak and brittle.

**Acknowledgment.** I thank Professor J. E. McIntyre and Dr. G. C. East of the University of Leeds, England, for helpful discussion. I gratefully acknowledge Contraves A. G., Switzerland, for making their rheological laboratory facilities available and the late Dipl.-Ing. Paul Brueggemann of Brueggemann Building and Construction Co., Duisburg, West Germany, for financial support.

**Registry No.** $BaO_2C(CH_2)_6CO_2$, 84223-46-1; $BaO_2C(CH_2)_8CO_2$, 19856-32-7; $BaO_2C(CH_2)_{10}CO_2$, 117020-95-8; $CaO_2C(CH_2)_6CO_2$, 27796-71-0; $CaO_2C(CH_2)_8CO_2$, 19455-80-2; $CaO_2C(CH_2)_{10}CO_2$, 30687-91-3; $MgO_2C(CH_2)_6CO_2$, 85561-39-3; $MgO_2C(CH_2)_8CO_2$, 19922-46-4; $MgO_2C(CH_2)_{10}CO_2$, 99932-62-4; $ZnO_2C(CH_2)_6CO_2$, 85561-38-2; $ZnO_2C(CH_2)_8CO_2$, 19856-33-8; $ZnO_2C(CH_2)_{10}CO_2$, 55489-75-3; $CdO_2C(CH_2)_6CO_2$, 34284-36-1; $CdO_2C(CH_2)_8CO_2$, 4476-04-4; $CdO_2C(CH_2)_{10}CO_2$, 117020-96-9; $PbO_2C(CH_2)_6CO_2$, 85561-40-6; $PbO_2C(CH_2)_8CO_2$, 29473-77-6; $PbO_2C(CH_2)_{10}CO_2$, 117020-97-0.

## References and Notes

(1) Economy, J.; Mason, J. H.; Wohrer, L. C. *Polym. Prepr.* **1966**, *7*, 596.
(2) Economy, J.; Mason, J. H.; Wohrer, L. C. *J. Polym. Sci., Polym. Chem. Ed.* **1970**, *8*, 2231.
(3) Economy, J.; Wohrer, L. C.; Mason, J. H. U.S. Patent 3657689, 1971, March 2.
(4) Economy, J.; Mason, J. H. In *Ionic Polymer*; Holliday, L., Ed.; Applied Science: London, 1975; p 261.
(5) Ibidapo, T. A., manuscript in preparation.
(6) Ibidapo, T. A.; Johnson, D. J. *Polymer* **1983**, *24*, 271.
(7) Oldham, C. In *Progress in Inorganic Chemistry*; Cotton, F. A., Ed.; 1968; Vol. 10, p 223.
(8) Bellamy, L. J. *The Infra-red Spectra of Complex Molecules*; Chapman and Hall: London, 1975; p 198.
(9) Kagarise, R. E. *J. Phys. Chem.* **1955**, *59*, 271.
(10) Nakamoto, K. *Infra-red Spectra of Inorganic Coordination Compounds*; Wiley: New York, 1963; p 197.
(11) Ubbelohde, A. R. *Ionic Liquids*; Inman, II, Lovering, B. G., Ed.; Plenum: New York, 1981; p 1.
(12) Wakelin, J. H.; Virgin, H. S.; Crystal, E. *J. Appl. Phys.* **1959**, *30*, 1654.
(13) Schultz, A. R. *Encycl. Polym. Sci. Technol.* **1966**, *4*, 331.

# Notes

## Solvent Partition Study in a Polymer Colloid Using Fluorescence Anisotropy Measurement

R. POPLI* and M. MCGLADE

*Louis Laboratory, S. C. Johnson & Son, Inc., Racine, Wisconsin 53403.* *Received April 27, 1988; Revised Manuscript Received July 11, 1988*

## Introduction

The fluorescence probe 1,6-diphenyl-1,3,5-hexatriene (DPH) has been extensively used to study order in lipid bilayers. The photophysical properties of DPH have been reviewed by Dale and Lakowicz.[1,2] The main advantage of DPH for these studies is the near colinearity of the absorption and emission dipoles and their alignment with the symmetry axis of the lipid bilayers. As a result, any change in the symmetry axis of the bilayer is easily detected.

A derivative of DPH with a cationic moiety affixed to the para position of one of the phenyl rings, 1-(4-(trimethylammonio)phenyl)-6-phenyl-1,3,5-hexatriene (TMA-DPH), was prepared by Prendergast et al.[3] The cationic moiety tethers the molecule at the lipid–water interface and the DPH part of the molecule is intercalated with the lipid.[3-5] The photophysics of TMA-DPH in the lipid bilayer was found to be similar to that of DPH.[3,6] TMA-DPH has extremely low solubility in water and its fluorescence activity in water alone is too low to be observable.[3,7]

In our studies, TMA-DPH was employed to examine changes in the local environment of the polymer colloid particles upon solvent addition. As in the case of lipid bilayers, it is assumed that the cationic end of the TMA-DPH molecule is located at the water–polymer interface and DPH part of the molecule is positioned among the polymer chains inside the polymer particle. Therefore, the anisotropy results reported here correspond to the local environment accessible to the probe molecule, which is estimated to be approximately 20–40 Å from the surface of the colloid particle.

The solvent added to the polymer colloid partitions between the aqueous and the polymer phases. The solvent partitioning into the polymer phase increases the mobility of the probe due to plasticization of the polymer. This change in the local environment is measured as a change in the fluorescence anisotropy of the TMA-DPH.

## Experimental Section

The polymer colloid used for this study is a dialyzed colloid

0024-9297/89/2222-1484$01.50/0 

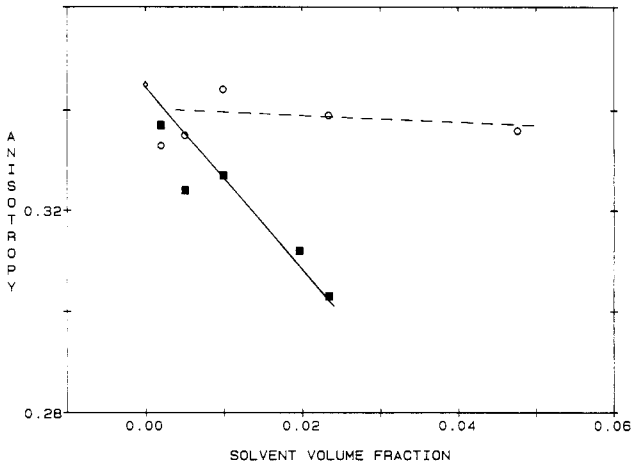


**Figure 1.** Changes in fluorescence anisotropy with concentration of the solvent added to the polymer colloid.

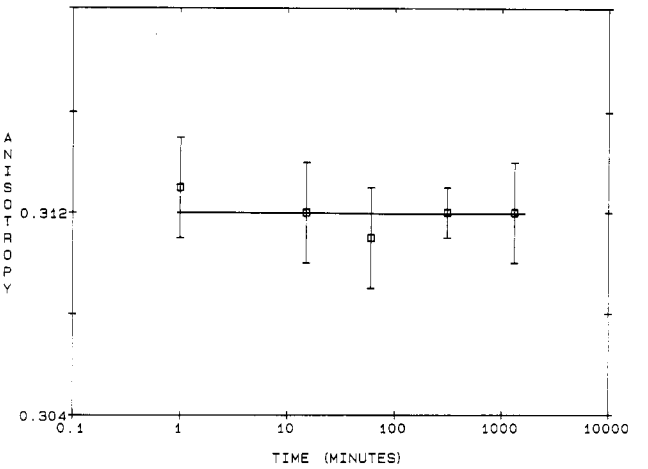


**Figure 2.** Changes in fluorescence with time after addition of the solvent, DEGBA, to the polymer colloid.

of a terpolymer of butyl methacrylate–butyl acrylate–methacrylic acid (BMA–BA–MMA). The colloid particle diameter is 76 nm and the particle size distribution is narrow, as measured by dynamic light scattering. The glass transition temperature ($T_g$) of the polymer colloid is measured to be approximately 20 °C by DSC.

The fluorescence probe TMA-DPH was obtained from Molecular Probes (Eugene, OR). A predetermined amount of a solution of TMA-DPH in acetone was transferred to a volumetric flask and acetone evaporated by passing a gentle stream of nitrogen gas over the surface. A sample of dialyzed polymer colloid of the terpolymer BMA–BA–MAA and deionized water were then added and the solution was allowed to stand in the dark for at least 1 day. The polymer concentration in the solution is 0.03% by weight. The TMA-DPH concentration in the solution is $3 \times 10^{-6}$% by weight. This corresponds to an average of approximately 30 TMA-DPH molecules per colloid particle. In preliminary experiments, it was determined that lowering the TMA-DPH concentration by a factor of approximately 8 had no effect on the measured anisotropy values. Solutions containing various concentrations of the solvents diethylene glycol butyl acetate (DEGBA) and diethylene glycol ethyl ether (DEGEE) were prepared to examine solvent partitioning between the polymer and the aqueous phases. The solvents were obtained from Tennessee Eastman and were used as obtained. GC analysis of the solvent showed no detectable impurities.

Fluorescence anisotropy measurements were made at 20 °C by using a SLM 4800S fluorimeter (SLM, Urbana, IL). Excitation and emission wavelengths were 352 and 453.8 nm, respectively. The emission wavelength was set by using an interference filter. Fluorescence anisotropy measurements were made by using two channels, T format geometry, to simultaneously measure the intensities of the parallel and perpendicular components. A detailed description of the technique has been given by Lakowicz.[8]

## Results and Discussion

The results of the anisotropy measurements for the solutions containing varying amounts of the two solvents are shown in Figure 1. These results clearly show a decrease in anisotropy with increasing solvent concentration for the solvent DEGBA and no change with concentration of the solvent DEGEE. The highest concentration of the solvent DEGBA used is close to its solubility limit in water. On the other hand, the solvent DEGEE is soluble in water at all concentrations.

The decrease in the anisotropy for DEGBA can be interpreted as an effect of the solvent partitioning into the polymer phase. A similar reasoning for the solvent DEGEE implies no partitioning of DEGEE to the polymer phase. These results are in agreement with independent observations of solvent partitioning in direct measurements employing determination of the solvent fraction in supernatants of the ultracentrifuged specimens.[9] The latter results were obtained at a much higher polymer colloid concentration. However, if we assume that the polymer colloid concentration has no effect on the solvent distribution; one would estimate that approximately 10% of the added DEGBA and 0% of the added DEGEE is present in the polymer particles in specimens of this study.

The anisotropy shift, according to the Perrin equation, can come from either a change in the rotational correlation time, due to a viscosity change of the local environment or a change in the fluorescence lifetime.[8] The anisotropy data alone do not allow a quantitative separation of two effects. However, a change in the anisotropy will be observed only if the local environment in the vicinity of the probe molecule inside the polymer particle is altered. This change in the local environment in the present situation can only come about as a result of solvent partitioning. Therefore, the observed anisotropy change irrespective of its nature, whether an effect of change in the rotational correlation time or the fluorescence lifetime, is a clear indication of solvent partitioning into the polymer phase.

Nevertheless, a study of the glass transition temperature ($T_g$) variation with the solvent concentration in polymer–solvent mixtures show a decrease in $T_g$ with increasing solvent concentration.[10] This would also mean a decrease in the viscosity of the solvent–polymer mixture with increasing solvent concentration. These results in conjunction with the discussion in previous paragraphs indicate that at least a part of the anisotropy decrease upon solvent addition to the polymer colloid is associated with a decrease in the viscosity of the probe environment.

In order to demonstrate that the partition measurements shown above represent thermodynamic equilibrium and that there are no time effects on the fluorescence of TMA-DPH, the kinetics of DEGBA partitioning into the polymer phase was examined. A measurement of the change in anisotropy of the solution with time after addition of the solvent to the polymer colloid/TMA-DPM mixture is shown in Figure 2. The shortest time wherein the anisotropy measurement could be done after solvent addition was 1 min. The experimental data, Figure 2, show that anisotropy reaches its equilibrium value in less than 1 min. Thus the kinetics of solvent partitioning for this system are extremely fast. This is not surprising considering that the polymer is almost above it glass transition temperature and that the particle distance over which the solvent must travel to give a change in anisotropy is nearly the length of the DPH molecule, approximately 20 Å.

## Conclusions

The solvent partitioning behavior between the polymer

and the aqueous phase can be seen from fluorescence measurements. However, a quantitative estimate of the solvent fraction in the polymer phase is difficult. The kinetics of solvent partitioning in the systems investigated is fast and is of the magnitude expected from the diffusion equation.

**Registry No.** DEGBA, 31353-26-1; DEGEE, 111-90-0; (butyl methacrylate)(butyl acrylate)(methacrylic acid) (copolymer), 30231-49-3.

## References and Notes


(1) Dale, R. E.; Chen, L. A.; Brand, L. *J. Biol. Chem.* **1977**, *252*, 7500.
(2) Lakowicz, J. R.; Prendergast, F. G.; Hogen, D. *Biochemistry* **1979**, *18*, 520.
(3) Prendergast, F. G.; Haugland, R. P.; Callahan, P. J. *Biochemistry* **1981**, *20*, 7333.
(4) Engel, L. W.; Prendergast, F. G. *Biochemistry* **1981**, *20*, 7338.
(5) Stubbs, C. D.; Kinosita, K., Jr.; Munkonge, F.; Quinn, P. J.; Ikegami, A. *Biochem. Biophys. Acta* **1984**, *775*, 374.
(6) Cundall, R. B.; Johnson, I.; Jones, M. W.; Thomas, E. W.; Munro, I. H. *Chem. Phys. Lett.* **1979**, *64*, 39.
(7) McGlade, M. J.; Randall, F. J.; Tcheurekdjian, N. *Macromolecules* **1987**, *20*, 1782.
(8) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum: New York, 1986.
(9) Popli, R.; Luccas, M. H.; Tsaur, S. L., manuscript in preparation.
(10) Popli, R.; Luccas, M. H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29* (June), 458.


## On the Sensitivity of Photoacoustic Fourier Transform Infrared Spectroscopy to Cross-Linking Reactions


MAREK W. URBAN* and SCOTT R. GABOURY

*Department of Polymers and Coatings, North Dakota State University, Fargo, North Dakota 58105.*


*Received April 8, 1988;*
*Revised Manuscript Received June 2, 1988*


Network formation, such as occurs during the curing of elastomers or thermosets, is a complex process that often forcloses the use of many analytical techniques to gain an understanding of the molecular architectures that develop. Since the measurements of macroscopic properties do not provide adequate information, one could propose at least a few spectroscopic methods to monitor the polymer network formation. However, the experimental difficulties or sensitivity may impose various limitations. In this contest, Fourier transform infrared (FT-IR) spectroscopy is no exception. Although we have a considerable interest in the development of this technique since it is a probe on a molecular level, the experimental difficulties in using it to evaluate the events during polymer network formation may cause some problems. While useful theoretical approaches (Gordon,[1] Mark,[2] Macosko,[3] and Eichinger[4]) have been developed, it is apparent that very little experimental work utilizing FT-IR was reported. Actually, this is not surprising if one analyzes the spectral changes that occur during the cross-linking process of hydroxyl-terminated poly(dimethylsiloxane) (PDMS, MW = 18000, Petrarch) with tetraethoxysilane (TES, Petrarch; catalyst, tin octoate). As seen in Figure 1, neither the intensity changes nor the appearance or disappearance of bands during various stages of curing is being observed. At this point it is necessary to raise the question as to why the cross-linking process cannot be detected by transmission measurements while the technique provides an adequate sensitivity to detect, for example, a compatibility of polymer

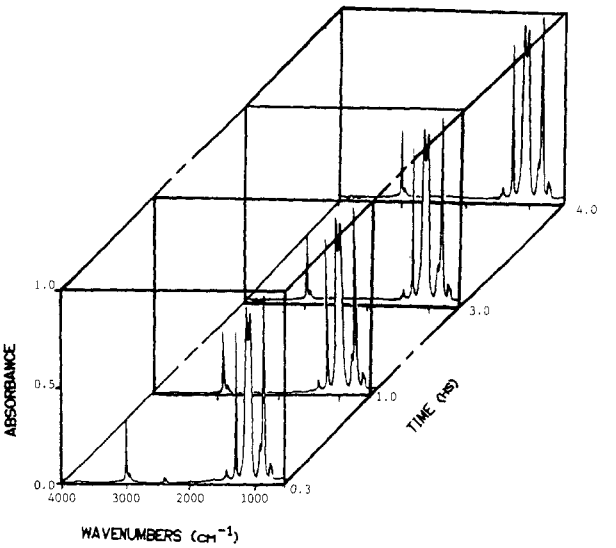


**Figure 1.** Transmission FT-IR spectra of PDMS/TES recorded at various stages of curing.

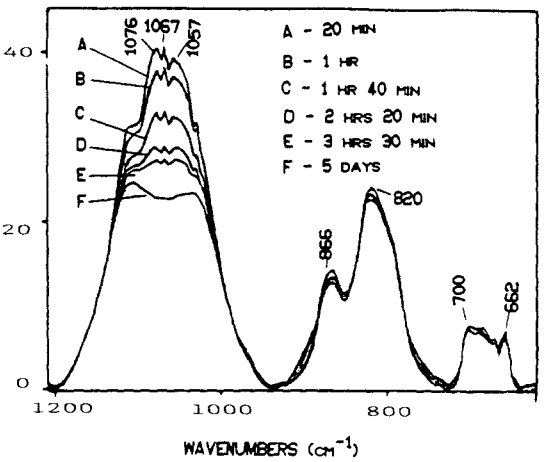


**Figure 2.** Photoacoustic FT-IR spectra of PDMS/TES recorded at various stages of curing.

blends.[5,6] One of the essential problems in cross-linking reactions is a small number of cross-links compared to the number of other bonds in the system. In addition, during the cross-linking of this particular system, the Si–OH bonds of PDMS and $H_5C_2$–O–Si of TES break to form the Si–O–Si network and ethanol. Thus, the simultaneous cleavage and formation of energetically similar bonds result in a heavy spectral overlap of strongly absorbing bands. Although one could monitor the disappearance of hydroxyl bands, their content is molecular weight dependent and, even with the relatively low molecular weights, their detection becomes impossible. Hence, in spite of the high sensitivity and speed of transmission FT-IR, this technique has an Achilles heel.

Let us examine the same cross-linking reaction by photoacoustic FT-IR spectroscopy. While the transmission FT-IR measurements do not provide sufficient sensitivity, the situation changes drastically when the same process is monitored photoacoustically. Figure 2 illustrates the spectral region from 1210 to 625 $cm^{-1}$ recorded as a function of time. It is clearly seen that the band at 1067 $cm^{-1}$, as well as other bands in the spectra, diminishes in intensity with time. On the other hand, the bands at 662 and 700 $cm^{-1}$ remain virtually unchanged as the reaction progresses. In order to provide a semiquantitative picture of the curing process, it is appropriate to compare the photoacoustic and transmission intensity changes plotted

0024-9297/89/2222-1486$01.50/0 