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# The use of 9-anthroic acid and new amide derivatives to monitorize curing of epoxy resins

O. Martin, J. Baselga*

*Department of Material Science, University Carlos III de Madrid, Leganés 28911, Spain*

**Abstract**

Curing of an epoxy resin was studied by steady-state fluorescence and correlationed with IR methods to get more insight on the physical processes occurring during the curing of an epoxy/amine system. We have synthesized and tested a set of 9-anthroic acid (AA) derivatives, that are sensitive to changes in the medium properties. Its fluorescenc response is analyzed and compared and it is concluded that *N*-dibutylanthroic acid amide shows the best performance.

**Keywords**

Epoxy resins; Curing; Fluorescence; 9-Anthroic acid

## 1. Introduction

Epoxy resins are a kind of thermosetting polymers based on the reaction between the epoxide precursor molecules themselves or on the reaction between the epoxy group and other kind of reactive molecules called hardeners with or without the help of a catalyst. Amines are one of the most im-portant agents used for curing of the epoxide resins. A large amount of work has been reported in the literature concern-ing the nature of the addition reaction between epoxides and amines [1–4]. Molecules containing single primary diamines give linear polymers when polymerized with diepoxides and the viscosity of the reaction mass increases consequently. If diamines or amine molecules containing higher functionality are used, joined with the increase of viscosity a cross-linked polymer is formed at a certain conversion (gel point). The liquid reaction mass becomes a solid and depending on polymerization temperature, the reaction may continue until all the monomer is exhausted or it may stop when diffu-sion of the different species becomes inhibited because of the very high viscosities achieved. This last phenomenon is called vitrificatio and the whole process is termed as curing. To follow the curing is an important industrial and fundamental issue because the physical and chemical prop-erties of the formed cross-linked polymer depend strongly on the achieved conversion, specially in the high con-version range.

The curing process is therefore a chemical process in which viscosity may change around six orders of magnitude. Kinetic studies on curing generally use infrared spectroscopy and differential scanning calorimetry, but these techniques are only sensitive to chemical conversion and not to viscosity. The viscosity increase during the curing process can be interpreted as a result of a decrease in the free volume fraction and some attempts have been reported to model the viscoelastic properties of the system during cure [5] in terms of Williams–Landel–Ferry semiempirical equation [6]. Nevertheless, molecular information is lacking from this approach and the fluorescenc of molecular labels can help to fil the gap. Fluorescent compounds in very low concentration have been used to probe molecular dynamics by chemically tagging them to the host molecule [7,8], to measure molecular orientation [9,10] and diffusion constants [11], and monitor polymerization [12] and the degree of cure of a curing thermoset material [13–15].

In a labeled system, as curing proceeds two main photophysical processes arise associated with the increase in viscosity. The reaction mass acts as a thermal bath for the excited fluorophore As monomers are assembled to form a cross-linked polymer there is a substantial reduction of trans-lational, rotational and vibrational degrees of freedom in the bath. Consequently, there is a reduction in the number of non-radiative deactivation pathways and an increase in flu-orescenc intensity is observed; small variations in the flu-orescenc envelope may be observed also. In certain cases, when there are at least two conformationally linked excited states in the same fluorophor that contribute to the overall emission (as in the case of TICT states), this restriction to

molecular motion may also perturb the population between the states. Consequently, relatively large variations in the shape of the fluorescenc spectra are observed.

9-Anthroic acid (AA) and its ester derivatives [16–22], are common fluorescenc dyes. In this work, we study amide derivatives of anthroic acid. The use of this kind of chromophores to monitor the curing process of epoxy resins is discussed.

## 2. Methods

*Fluorescence dyes*, *materials*, *synthesis and characterization*. AA, *n*-butyl amine, di-*n*-butyl amine and all solvents were purchased from Aldrich. AA was purifie dissolving it in a base following by precipitation with acid and recrystallization in ethanol. Thionyl chloride was added to a solution of AA in dichloromethane, stirred at reflu for 24 h, then evaporated to dryness and washed finall with dichloromethane. The resulting acid chloride was dissolved in chloroform and a solution of *n*-butyl amine or di-*n*-butyl amine in each case was added. The solution was reflu ed for 1 h. The reaction mixture was washed with 1 N aqueous sodium hydroxide and water. The products, *N*-butylamide 9-anthroate (BA) and *N*-dibutylamide 9-anthroate (DBA), Fig. 1, were purifie by chromatography to give yellow, BA, or orange, DBA, crystalline products. Single spots were obtained on TLC and only one peak in GPC with fluorescen detection. The product was characterized by $H^1$ MNR. BA: $\delta = 8.3$ (1H, s), $\delta = 7.85$ (4H, m), $\delta = 7.3$ (4H, m), $\delta = 7.1$ ($CDCl_3$), $\delta = 5.9$ (1H, s), $\delta = 3.5$ (2H, q), $\delta = 1.55$ (2H, q), $\delta = 1.32$ (2H, m), $\delta = 0.81$ (3H, t). DBA: $\delta = 8.55$ (1H, s), $\delta = 8.10$ (4H, m), $\delta = 7.55$ (4H, m), $\delta = 7.40$ ($CDCl_3$), $\delta = 3.87$ (2H, t), $\delta = 3.00$ (2H, t), $\delta = 2.00$ (2H, q), $\delta = 1.65$ (2H, m), $\delta = 1.38$ (2H, q), $\delta = 1.18$ (3H, t), $\delta = 0.90$ (2H, m) $\delta = 0.48$ (3H, t).

Table 1 shows the photophysical parameters obtained for all the dyes in THF.

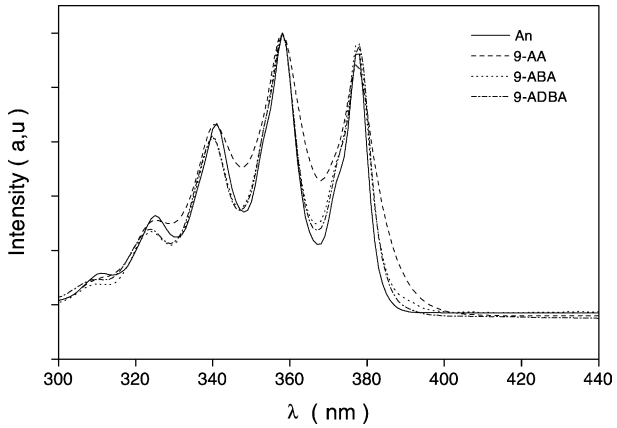



Fig. 2. Absorption spectra of An, AA, BA and DBA in THF.

*Epoxy resin*. Two different commercial epoxy resins, ER1 and ER2, were used. The epoxy formulations were supplied by Gairesa (Spain) in the form of a two component formulation. The principal constituents were bisphenol A diglycidyl ether (DGEBA), as firs component for both resins, and 1,4-dicyclohexyl diamine or a solution of *meta*-xylene diamine in alcohol as the second component for ER1 and ER2, respectively. Three-gram solution of dyes (AB, AA or DBA) in THF ($\approx 10^{-5}$ M) were mixed with 10 g of resin (firs component). THF was vacuum evaporated at 60 °C. The second component was mixed and reaction started. The reactive mixture was injected with a syringe between two glasses (1.2 mm), separated by a 1 mm Teflo spacer, at ambient temperature. The fluorescenc and IR spectra were recorded every hour during 20 h.

## 3. Results and discussion

Absorption spectra of anthracene (An), AA, BA and DBA in THF are shown in Fig. 2. The electron donating character

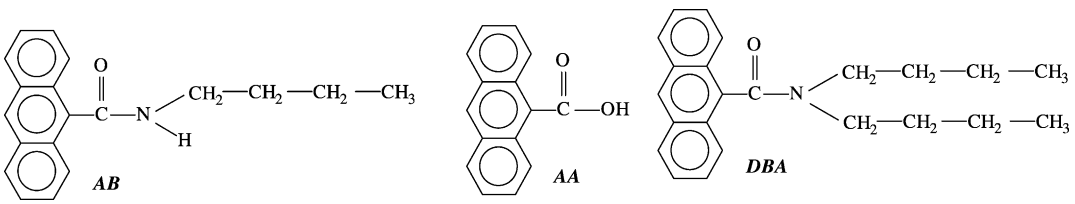



Fig. 1. Chemical structure of 9-anthroic derivatives: AA, AB and DBA.

Table 1
Photophysical parameters of dyes, AA, BA and DBA

| | AA | BA | DBA |
|---|---|---|---|
| $\varepsilon$ ($\times 10^5$ mol$^{-1}$ l cm$^{-1}$) | $0.075 \pm 10^{-3}$ | $0.05 \pm 10^{-3}$ | $0.001 \pm 10^{-3}$ |
| $\phi_{THF}$ | $7.03 \pm 1$ | $1.15 \pm 0.5$ | $2.7 \pm 10^{-1}$ |
| $\lambda_{max}$ (exc)/$\lambda_{max}$ (em) | 361/459 | 361/412 | 361/409 |

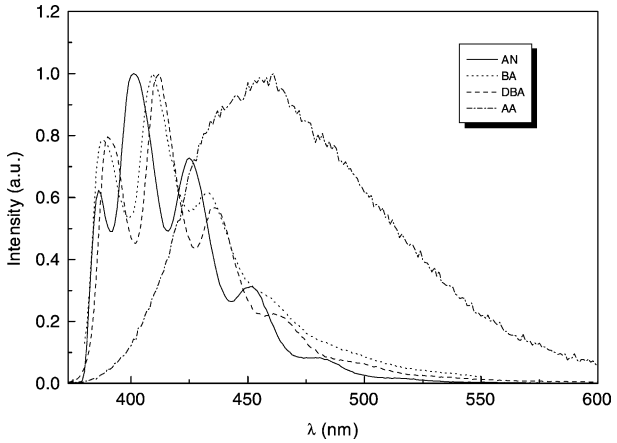



Fig. 3. Emission spectra of An, AA, BA and DBA in THF.

of the substituent group increases the displacement of the absorption spectrum to the blue respect to the An absorption spectrum. This behavior is similar for all the studied compounds. The emission spectra of An, AA, BA and DBA in THF are shown in Fig. 3. BA and DBA have similar spectra than An in different solvents, they conserve the vibrational structure and the specular image respect to the excitation spectra. AA has different compartment than BA and DBA in aprotic solvent. A Stokes-shift displacement and losses of the vibrational structure is slow. In hydroxyl solvent, depending of the concentration the emission is similar to BA and DBA.

## 4. Cure monitoring by fluo escence

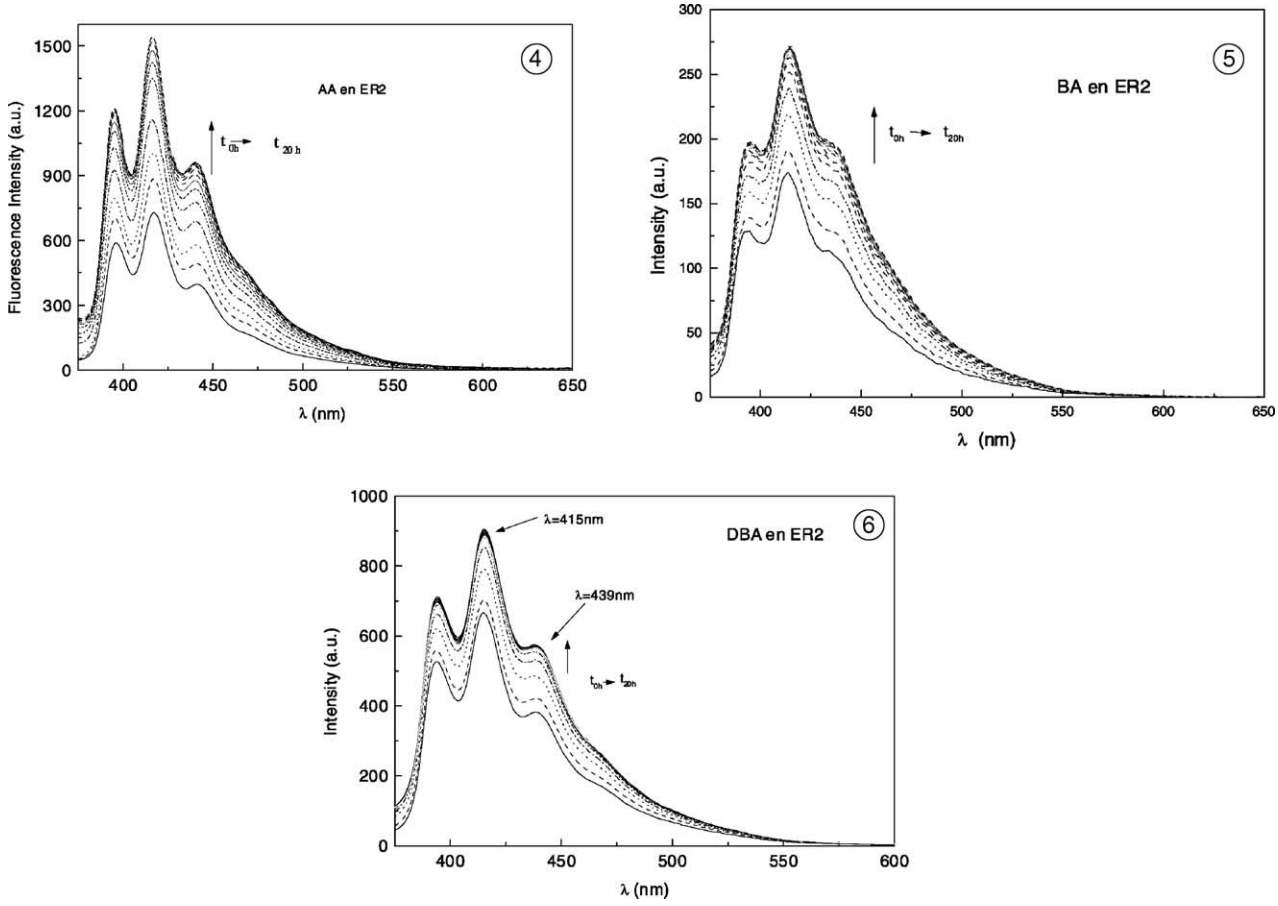
We follow the resin curing by fluorescenc recording the emission spectrum every 50 min. Figs. 4–6 represent the results for the different dyes in ER2 resin, all of them have the same vibrational structure as An. Fluorescence intensity increases with curing time reflectin that the viscosity of the reaction mixture increases also.

Nevertheless, when the ER1 resin is used, Figs. 7–9, the spectra are different for each dye.

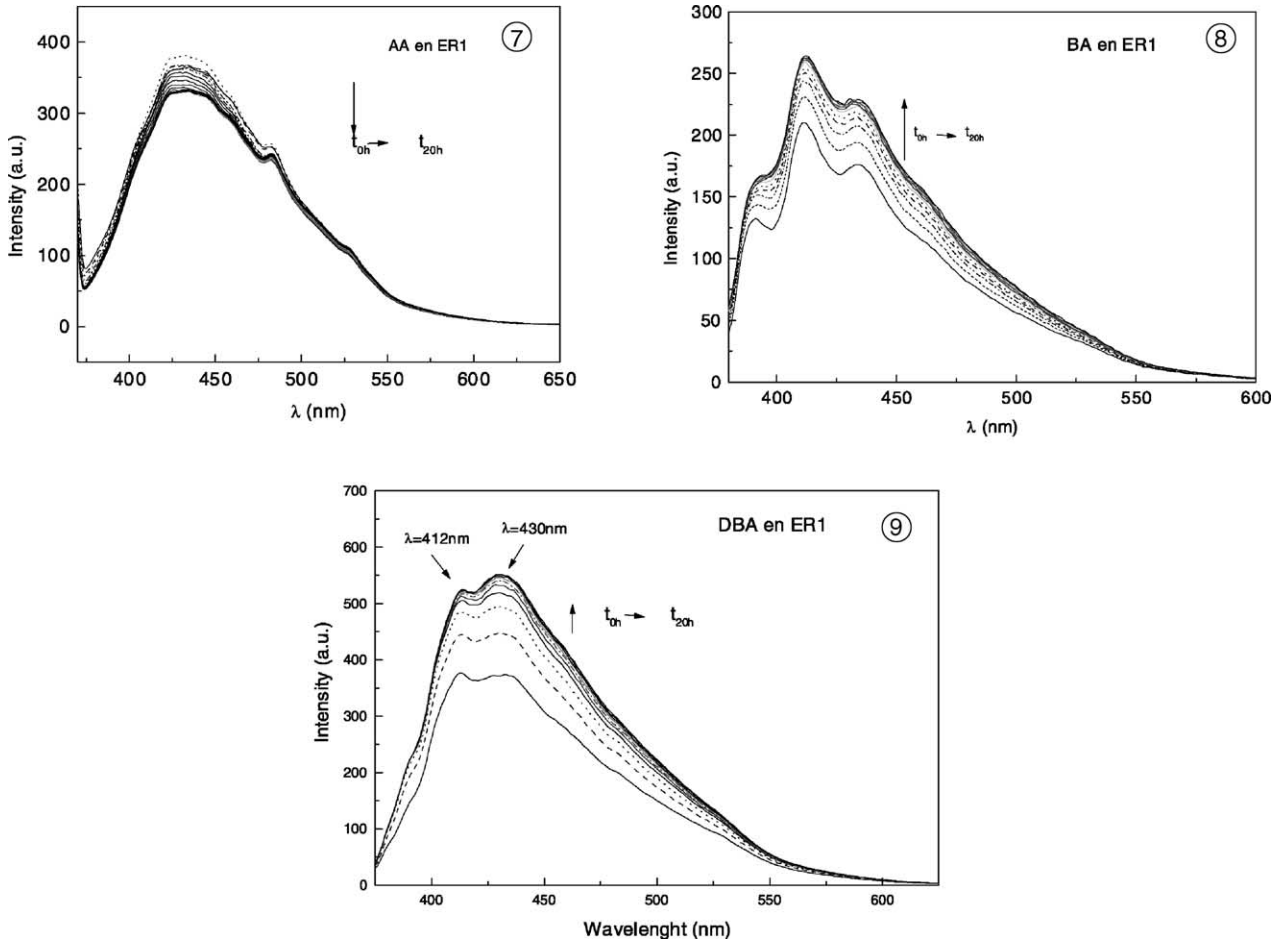
Only BA presents the same behavior in ER1 and ER2 resins; DBA loses its firs vibrational band and AA shifts to higher wavelengths losing its vibrational structure also.

## 5. Cure monitoring by near-IR

Epoxy and amine groups have a very characteristic near-infrared peaks [23], primary amine at 4941 $cm^{-1}$ and the epoxy group at 4527 $cm^{-1}$. The dyes inserted in




Figs. 4-6. Fluorescence emission response of AA, BA and DBA each 50 min during curing of ER2 epoxy resin.




Figs. 7-9. Fluorescence emission response of AA, BA and DBA each 50 min during curing of ER1 epoxy resin.

the epoxy resin matrix are in a very low concentration ($\approx 10^{-6}$ M) so we can preclude its interference with the curing process. During the curing the primary amines and the epoxy groups disappear, appearing at firs the secondary amine signal that disappears when it is converted into tertiary amine at the end of the addition process. So, if the relative area of epoxy and amine bands is followed during the curing, it is possible to calculate the concentration profil with the progress of curing. Fig. 10 shows the composition of several IR spectra along the curing process for ER2 resin.

Epoxy ($\alpha$) and amine ($\beta$) conversion were calculated according to the following equations.

$$\alpha(\nu = 4935\,\mathrm{cm}^{-1}) = \frac{\oint_{t_0} - \oint_t}{\oint_{t_0}},$$

$$\beta(\nu = 4530\,\mathrm{cm}^{-1}) = \frac{\oint_{t_0} - \oint_t}{\oint_{t_0}}$$

Results are shown in Fig. 11.

Epoxy or amine conversion can be correlated with fluo rescence intensity at different curing times. Fig. 12 presents such correlation for DBA probe in the ER1 epoxy resin. A linear variation between conversion and fluorescenc parameters can be clearly observed.

If instead of fluorescenc intensity the ratio between two emission maxima are plotted against conversion additional information can be obtained. These results are presented in Fig. 13, where it can be observed a change of slope at around 45% conversion.

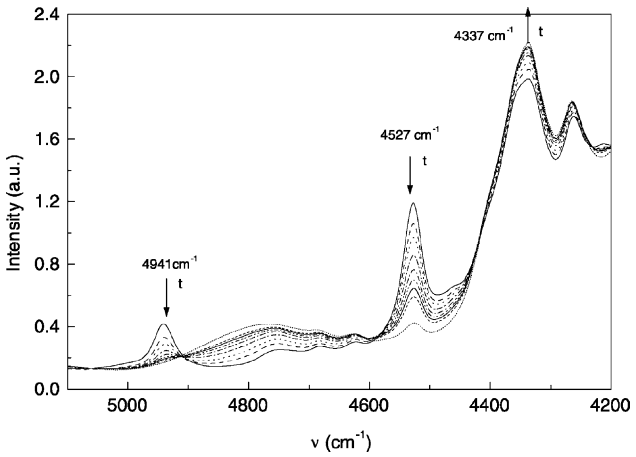



Fig. 10. Near-IR spectra of ER2 resin during the curing process. Each spectra is taken every 50 min.

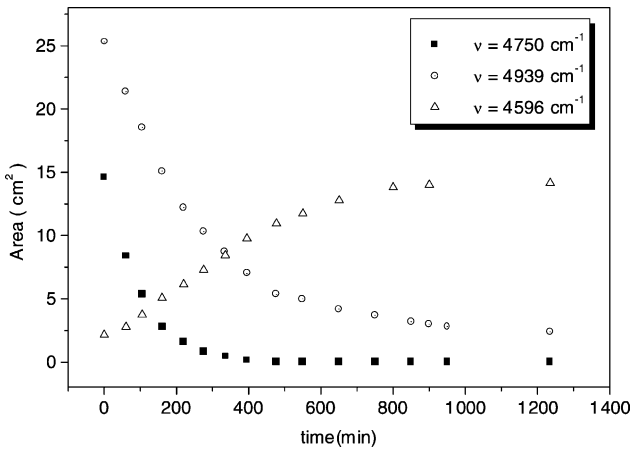



Fig. 11. Area changed each 50 min during curing of ER1 epoxy resin at different frequencies.

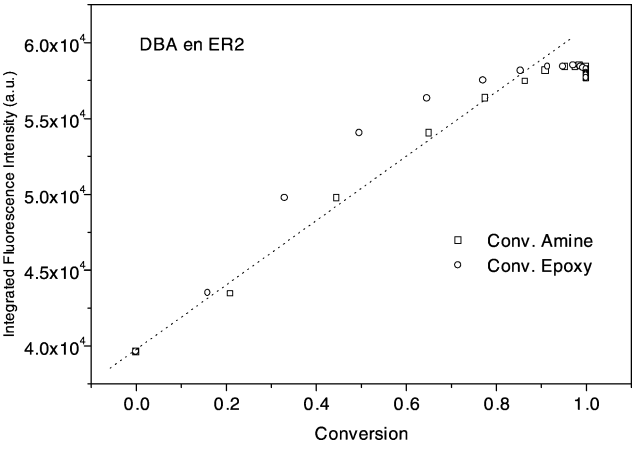



Fig. 12. Correlation between fluorescenc intensity of DBA with amine and epoxy conversion for ER1 epoxy resin.

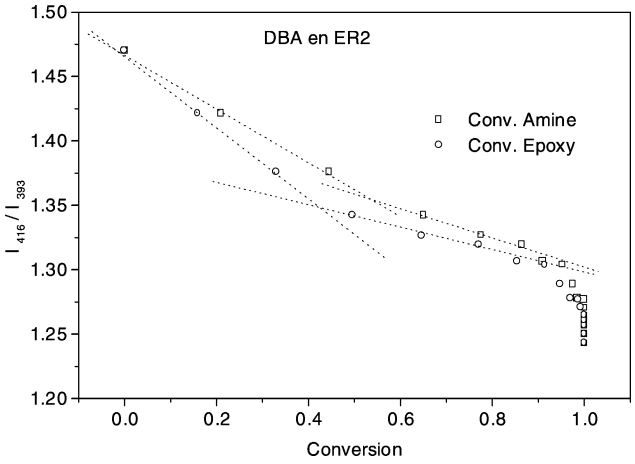



Fig. 13. Ratio of fluorescenc intensity at 416 and 393 nm of DBA against conversion of amine and epoxy for ER1 epoxy resin.

## 6. Conclusions

- When the viscosity of the medium increases there is a proportional increase in fluorescenc yield of the three tested dyes in ER2 and only DBA presents this behavior in ER1 resin, probably associated with the absence of hydrogen bonding ability.
- In ER2 resin all dyes change its vibrational structure during the cure process and this change is not linear. At a conversion around 45% a change in the system is observed. The proximity of the gel point suggests that these dyes can be used to determine the gel point of the resins.
- We conclude that the more interesting dye for this kind of resins is the DBA.

## References

[1] L. Shechter, J. Wynstra, R.E. Kurkjy, Ind. Eng. Chem. 48 (1956) 94.
[2] T. Kakurai, T. Noguchi, J. Soc. Org. Synth. Chem. Jpn. 18 (1960) 485.
[3] H.A. Newey, Paper Presented at the Gordon Research Conference on Polymers, New London, Conn., July 8, 1955.
[4] J.C. Illman, Paper Presented at SPE Technology Conference, Montreal, 1966;
J.C. Illman, J. Appl. Polym. Sci. 10 (1966) 1519.
[5] M.L. Williams, R.F. Landell, J.D. Ferry, J. Am. Chem. Soc. 77 (1955) 3701.
[6] (a) D.J. Plazek, I.-C. Chay, J. Polym. Sci. 29 (1991) 17;
(b) S.L. Simon, G.B. Mckenna, O. Sindt, J. Appl. Polym. Sci. 76 (2000) 495.
[7] T. Sasaki, M.Y. Yamamoto, Y. Nishijima, Macromolecules 21 (1988) 610.
[8] B. Valeur, L. Monerie, J. Polym. Sci. 14 (1976) 11.
[9] J.P. Jarry, L. Monnerie, J. Polym. Sci. Polym. Phys. Ed. 18 (1980) 1879.
[10] D.I. Bower, K.K.P. Korybut-Daszkiewicz, I.M. Ward, J. Appl. Polym. Sci. 28 (1983) 1195.
[11] F.W. Wang, E. Wu, Polym. Commun. 28 (1987) 73.
[12] F.W. Wang, R.E. Lowry, W.H. Grant, Polymer 25 (1984) 690.
[13] F.W. Wang, R.E. Lowry, B.M. Fanconi, Polymer 27 (1986) 1529.
[14] F.W. Wang, R.E. Lowry, W.J. Pummer, B.M. Fanconi, E. Wu, in: C.E. Hoyle, J.M. Torkelson (Eds.), Photophysics of Polymers, ACS Symposium Series 358, American Chemical Society, Washington, DC, 1987, Chapter 33, p. 454.
[15] R.L. Levy, Polym. Mater. Sci. Eng. 50 (1984) 124.
[16] T.C. Werner, D.M. Hercules, J. Phys. Chem. 74 (5) (1970) 1030.
[17] T.C. Werner, R.M. Hoffman, J. Phys. Chem. 77 (13) (1973) 1611.
[18] S. Suzuki, T. Fujii, N. Yoshiike, S. Komatsu, T. Iida, Bull. Chem. Soc. Jpn. 51 (9) (1978) 2460.
[19] C.S.P. Sung, N.H. Sung, Mater. Sci. Eng. A 162 (1993) 241.
[20] R. Agbaria, M. Butterfield I.M. Warner, J. Phys. Chem. 100 (43) (1996) 17133.
[21] V. Swayambunathan, E.C. Lim, J. Phys. Chem. 91 (25) (1987) 6359.
[22] J.L. Dey, I.M. Haynes, A.K. Warner, Chandra, J. Phys. Chem. 101 (1997) 2271.
[23] S. Paz-Abuin, A. Lopez-Quintela, M. Varela, M. Pazos-Pellin, P. Prendes, Polymer 12 (1997) 3117.