Unsaturated polyester–styrene resins: Effect of the catalyst concentration on the kinetic rate and activation energy of the radical crosslinking reactions

Maurizio Paci* and Francesco Campana†
Department of Chemistry, University of Rome 'La Sapienza', P.za A. Moro 5, I-00185 Rome, Italy

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The T_1 spin lattice relaxation time, measured by pulsed n.m.r., has been used to monitor the effect of the catalyst concentration on the kinetics of the radical crosslinking reaction of unsaturated polyester–styrene resins. The measurements were performed primarily in the intermediate–final part of the reaction under isothermal conditions. The loss of mobility of the protons of the sample has been correlated with the degree of cure and the kinetic constant as well as with the activation energy, and has been evaluated using the semi-empirical kinetic expression proposed by Kamal *et al.* In the concentration range investigated (from 0.05 to 0.3% w/w) for the catalyst cobalt octanoate the decrease of the activation energy for the process was found to be 2.3 kcal mol^{-1} of double bonds for each 0.1% w/w of cobalt octanoate.

(Keywords: polyester–styrene resins; n.m.r.; radical crosslinking reaction; kinetics)

INTRODUCTION

Polyester resins finding widespread technological applications are commonly prepared by mixing unsaturated polyesters and styrene in weight ratios which ensure a nearly complete reaction of polyester and styrene double bonds when the resin is crosslinked by means of radical processes (cure).

Typical polyesters are prepared by polycondensation of maleic and phthalic anhydrides and glycols. The polymer, thus obtained, contains fumarate residues, owing to the occurrence of the *cis–trans* isomerization of the maleic residues, which are able to react with the added styrene monomers via a radical reaction[1].

Styrene units and/or styrene bridges link different polyester chains, thus giving rise to a three dimensional network[2].

In our laboratory the spin–lattice relaxation time T_1[3] of the protons of the resin were measured during the course of the curing process under isothermal conditions and at a frequency of 20 MHz[4]. Pulsed n.m.r. has been shown to be a useful technique[5], in the characterization and monitoring of the cure kinetics of different type of resins.

The results of these studies indicate that pulsed n.m.r. studies of the cure of unsaturated polyester resins would be informative, since it would enable the loss of general molecular mobility of the system to be determined during the formation of the three-dimensional network due to the crosslinking reaction.

This paper reports the results of a pulsed n.m.r. study of the cure process of unsaturated polyester resins at different concentrations of the catalyst cobalt octanoate in order to elucidate the influence on the kinetic constants of the cure as well as on the activation energy of the entire process.

EXPERIMENTAL

The resin under study comprises an unsaturated polyester obtained by polycondensation from maleic anhydride (AM), phthalic anhydride (AP) and dipropylene glycol (DPG) in a molar ratio AM:AP:DGP = 0.2:0.8:1.0 and styrene 28% w/w.

Methyl ethyl ketone peroxide (0.5% w/w) was used as initiator, and cobalt octanoate at different concentrations (i.e. 0.05, 0.2 and 0.3% w/w) as catalyst.

The resin (approximately 100 g) was initiated in a glass beaker stirring vigorously for about 30 s. An amount was transferred into a 10 mm glass tube (external diameter) for the n.m.r. measurements.

T_1 relaxation times were measured by the 180–τ–90 pulse sequence with a waiting time of 10 s as an average of ten sequences on a Bruker Minispec P20 instrument operating at 20 MHz.

The temperature was held constant (± 1°C) by means of a rapid flow of thermostatting liquid in the probe jacket; cure was followed at 41°C, 51°C and 64°C.

Measurements were performed every 15 min, for 1 h, and every 30 min, for 8–9 h. The final values were obtained after 24 h from the addition of the initiator.

RESULTS AND DISCUSSION

A typical magnetization–time decay plot of $\ln(M_\infty - M_\tau)$ vs. τ is shown in *Figure 1* at different elapsed times from the initiation of the radical reaction. The values show a non-exponential behaviour due to presence in the sample

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* Permanent address: Department of Chemistry, University of Rome 'Tor Vergata', 00173 Rome, Italy.

† Permanent address: SNIAL SpA, Colleferro, 00034 Roma, Italy

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of both fast and slow relaxing components. The former disappears as the cure reaction proceeds, this observation suggests that there are separate behaviours of the protons of the sample from a mobility point of view. During the cure reaction the T_1 of the slow relaxing component changes with time increasing asympotically to a final value. As one can see in *Figures 2a, b* and *c* this behaviour is influenced by the temperature and by the different concentration of the cobalt octanoate catalyst. In all cases the rate of the T_1 changes markedly thus indicating a large effect of these parameters (temperature and catalyst concentration) on the efficiency of the cure process.

The T_1 variation should be attributed to the decrease in the general molecular mobility associated with the formation of the three-dimensional network built up by the crosslinking reaction.

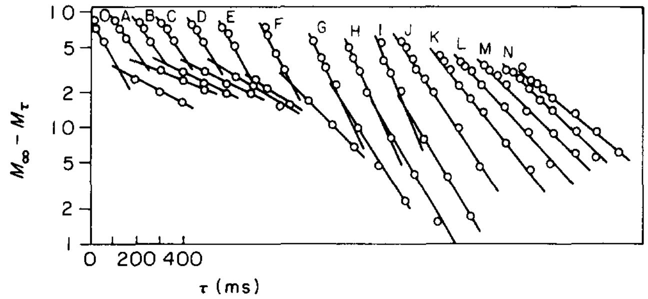

Figure 1 Typical magnetization decay plot as a function of τ time in the 180–τ–90 pulse sequence at different elapsed times of the cure from the initiator addition. Letters indicate the time reaction: O = 0.0 min: A = 15; B = 30; C = 45; D = 60; E = 90; F = 120; G = 150; I = 180; J = 240; K = 300; M = 420; N = 480; O = 1440. τ values are reported and referred only to the curve for $t = 0.0$

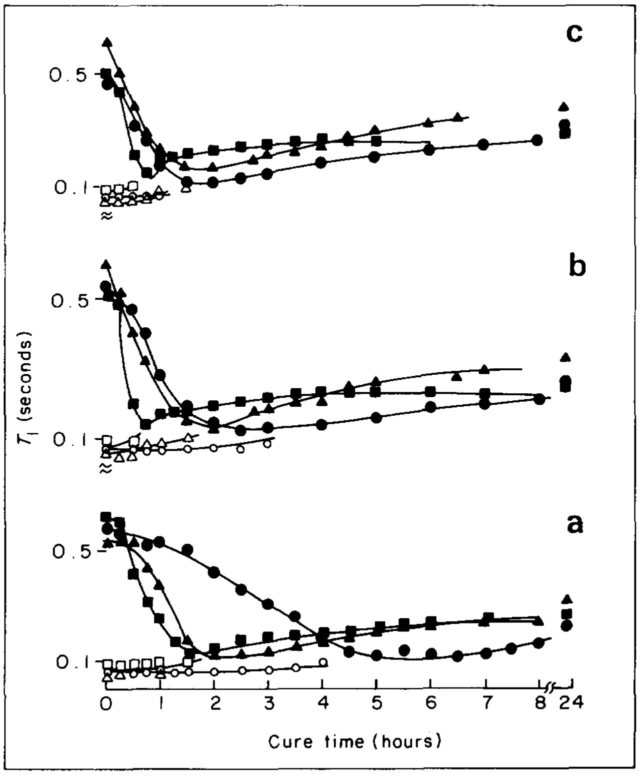

Figure 2 Spin–lattice relaxation time T_1 of the proton in the resin sample during the cure reaction at 41°C, 51°C and 64°C (●, ▲, ■ respectively); Open symbols refer to the fast relaxing component, a, b and c indicate different concentrations of cobalt octanoate catalyst in the resin (0.05, 0.2 and 0.3% w/w respectively)

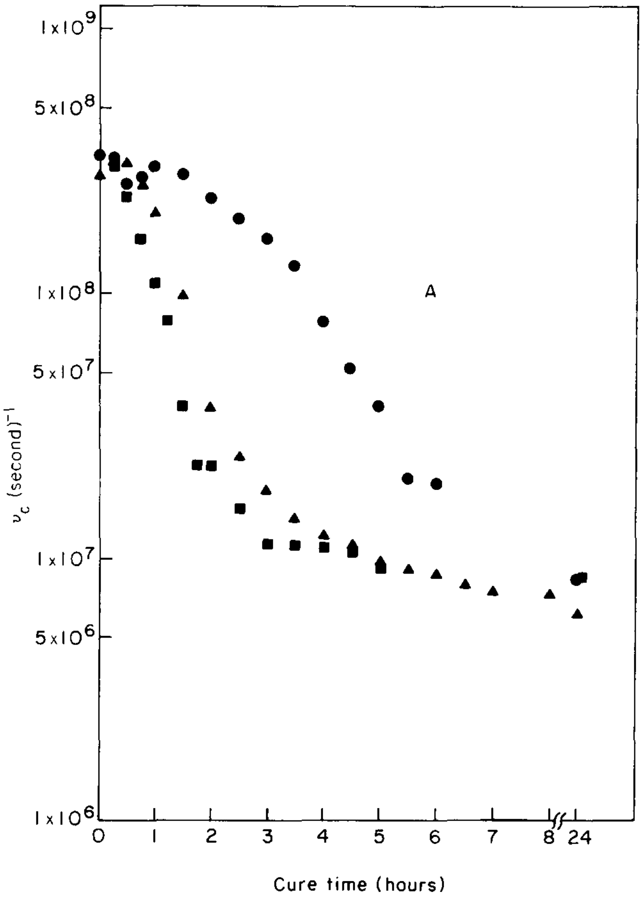

Figure 3 Dependence of the correlation frequency ν_c of the general molecular motion, obtained from the T_1 relaxation time of the slow relaxing component as in *Figure 1*, as a function of the cure time for the resins containing different amounts of catalyst cobalt octanoate. Only the 0.05 w/w concentration is reported (A). Symbols indicate different temperatures as in *Figure 2*

Using the well-known dependence of the T_1 value on the correlation frequency of the molecular motion[6,7] the loss of general mobility in the resin in the course of the radical process can be obtained. In *Figure 3* is reported, as an example, the decrease in the correlation frequency of the general molecular motion during the time evaluated from the T_1 reported in *Figure 2a.*

Considering the values of the correlation frequency of the molecular motions in both the initial and final states a fractional loss of mobility, α, during the cure, can be evaluated as a function of the time as reported in *Figures 4a, b* and *c* for the three samples examined.

The kinetic expression for the autocatalytic isothermal cure process, proposed by Kamal *et al.*[8a,b] was proved to be in good agreement in such a system[9]:

$$\left(\frac{d\alpha}{dt}\right) = (K_1 + K_2\alpha^m)(1-\alpha)^n$$

Assuming that K_1 is very close to zero, as found in several cases[10], the slope of the α vs. t curve measured for $\alpha = 0.5$ can give directly the K_2 value:

$$\left(\frac{d\alpha}{dt}\right)_{\alpha=0.5} = K_2(0.5)^{m+n}$$

where $m+n$ is generally considered equal to 2 for the second order cure reaction. Thus the kinetic constant for the crosslinking reaction for the intermediate–final stage of the cure can be obtained. The K_2 values are reported in

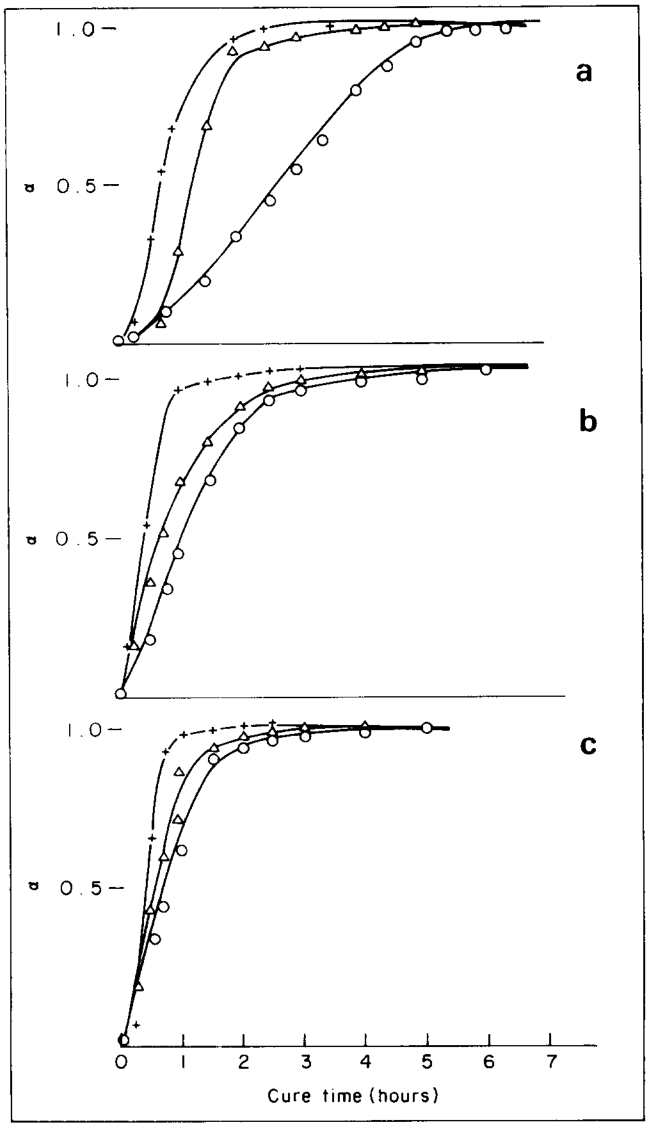

Figure 4 Fractional loss of molecular mobility interpreted as a measure of the degree of crosslinking in resins containing different amounts of catalyst cobalt octanoate as in *Figure 3*. Symbols refer to the temperature of the cure as reported in *Figure 2*

Table 1 for the different concentrations of cobalt octanoate used.

The Arrhenius relationship gives directly the apparent activation energy E_a of the cure process. In *Figure 5* one can see the dependence of the activation energy value on the concentration of the catalyst used.

The straight line behaviour observed indicates that, at least in the concentration range investigated and under our experimental conditions, the apparent activation energy of the cure decreases by about 2.3 kcal mol^{-1} of double bonds for each 0.1% of cobalt octanoate added to the resins.

In conclusion pulsed n.m.r. has been shown to be a useful technique for following and characterizing the crosslinking kinetics of styrene unsaturated polyester systems.

Further work is in progress to evaluate the effects on the kinetic parameters of various additives, e.g. low profile agents, as well as the presence of reinforcing agents and fillers.

Table 1 Kinetic constants for the intermediate–final stage of the cure of unsaturated polyester resins at different temperatures and in the presence of different concentrations of catalyst cobalt octanoate

	K_2 kinetic constant (min^{-1} mol^{-1})[a]		
T (°C)	Co octanoate 0.05% w/w	Co octanoate 0.2% w/w	Co octanoate 0.3% w/w
41	0.030	0.054	0.084
51	0.046	0.107	0.132
64	0.131	0.187	0.200

[a] Per mole of double bonds in the resin

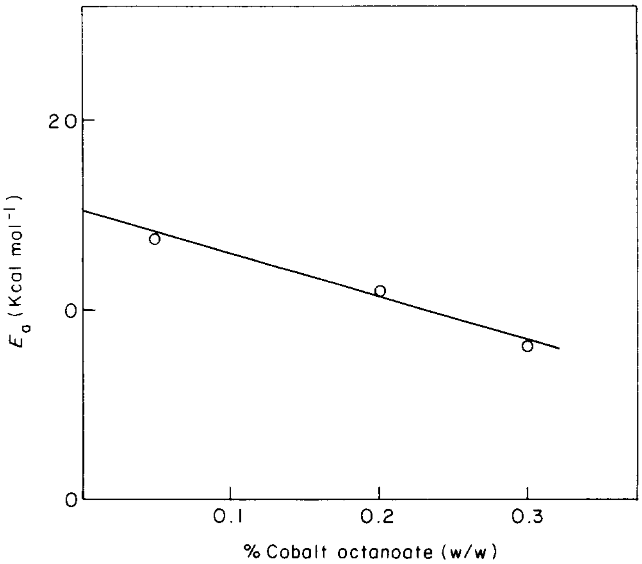

Figure 5 Dependence of the apparent activation energy E_a on the concentration of the catalyst cobalt octanoate, expressed in % w/w per double bond in the unsaturated polyester–styrene resin

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