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Fast transient fluorescence (FTRF) technique for monitoring free-radical crosslinking copolymerization (FCC) of styrene (S) with various divinylbenzene (DVB) contents

Ö. Pekcan*, D. Kaya

Istanbul Technical University, Department of Physics, Maslak, 80626 Istanbul, Turkey

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Abstract

The gelation during free-radical crosslinking copolymerization (FCC) of styrene (S) and commercial divinylbenzene (DVB) in bulk was studied using Fast Transient Fluorescence (FTRF) technique. Pyrene (Py) was used as a fluorescence probe for the FTRF experiments. Fluorescence lifetimes of Py from its decay traces were measured and used to monitor the gelation processes in various DVB contents. Styrene consumption rates were measured during gelation process employing Stern-Volmer kinetic model. Composite rate constants, k_r were determined for each DVB content experiments and it is observed that as DVB is increased k_r increases. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Fluorescence; Lifetimes; Gelation

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1. Introduction

Free-radical crosslinking copolymerization (FCC) has been widely used to synthesize polymer gels. Several theories have been developed in the past half century to describe gel formation in FCC, among which percolation theory provides a basis for modeling sol–gel phase transition [1–3]. Another type of theories called mean-field theories such as the statistical and kinetic theories bases on a 'tree approximation'. Statistical theories originate from Flory [4] and Stockmayer [5] models which assume equal reactivities of functional groups in the absence of cyclization reactions. In FCC, the formation of bonds building the network can be described using differential equations with reaction time or monomer conversion as the independent variable. The kinetic approaches can take into account all the kinetic features of copolymerization and crosslinking reactions which may suggest a more realistic approach to the mechanism of gelation process [6–9]. Kinetic models have been extensively used to describe the relations between the molecular weight of polymer and the conversion or reaction time during crosslinking process. In the classical kinetic theory, the rate constant is proportional to the product of the number functional groups in each reactant.

Because of its long excited singlet lifetime, pyrene (Py) as a chromophore [10] is an attractive choice for studying dynamics in polymers. P_y has been successfully employed as the fluorescence probe in the study of micellar [11] and phospholipid dispersions [12]. These studies focus on the use of dynamics of quenching of P_y monomer fluorescence and excimer formation processes. The other application of the use of P_y as a fluorescence probe is the study of the vibronic fine structure of its monomer fluorescence. The intensities of the various vibronic bands show a strong dependence on the solvent environment [13]. In the presence of polar solvents there is an enhancement in the intensity of the 0–0 band whereas there is a little effect on other bands; thus the ratio of intensities of these bands has been used to study environmental change. For about two decades the transient fluorescence (TRF) technique for measuring fluorescence decay has been routinely applied to study many polymeric systems using dyes both as a probe and/or as labels [14–18]. TRF spectroscopy with direct energy transfer (DET) and quenching method has been used to characterize internal morphologies of composite polymeric materials [19,20]. Quenching besides, DET is the general word used to describe any bimolecular process, which decreases the emission decay rate. The most important feature of these quenching mechanisms involves inter-

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* Corresponding author. Tel.: +90-0212-285-3213; fax: +90-0212-285-6366.

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actions between groups over different interaction distances. A single-photon counting (SPC) technique which produces decay curves and measures lifetimes in conjunction with DET was used to study the diffusion of small dye molecules within the interphase domain of anthracene and/or phenanthrene labelled poly(methyl methacrylate) (PMMA) particles [21]. Pyrene derivative was used as a fluorescence molecule to monitor the polymerization, aging and drying of aluminosilicate gels [22]. These results were interpreted in terms of the chemical changes occurring during the sol–gel process and the interactions between the chromophores and the sol–gel matrix. We reported in situ observations of the sol–gel phase transition in free-radical crosslinking copolymerization using the steady-state fluorescence (SSF) technique [23–28]. Recently fast transient fluorescence (FTRF) technique was used to study dissolution of polymer films and swelling of gels in our laboratory [29–31].

In this paper, a particular type of FTRF, the strobe technique, was used to study the sol–gel transition in FCC of styrene (S) and divinyl benzene (DVB). The major advantage of the strobe technique over other lifetime instruments is the time duration of a single experiment, which takes only seconds. In this work, this advantage of strobe technique was employed to make at least 20–30 lifetime measurements during the gelation of S with DVB, over a time interval of 1 h. In-situ, FTRF experiments were carried out by illuminating the sample cell during gelation, and fluorescence decay traces were observed using the Strobe Master System (SMS). The Stern-Volmer quenching equation was employed to monitor S consumption during the sol–gel phase transition in various DVB content samples.

2. Fluorescence quenching

Fluorescence intensities of aromatic molecules are affected by both radiative and non-radiative processes [32]. If the possibility of perturbation due to oxygen is excluded, the radiative probabilities are found to be relatively independent of environment and even of molecular species. Environmental effects on non-radiative transitions that are primarily intramolecular in nature are believed to arise from a breakdown of the Born-Oppenheimer aproximation [33]. The role of the solvent in such a picture is to add the quasi-continuum of states needed to satisfy energy resonance conditions. The solvent acts as an energy sink for rapid vibrational relaxation that occurs after the rate limiting transition from the initial state. Years ago, Birks et al. studied the influence of solvent viscosity on fluorescence characteristics of pyrene solutions in various solvents and observed that the rate of monomer internal quenching is affected by solvent quality [34]. Weber et al. reported the solvent dependence of energy trapping in phenanthrene block polymers and explained the decrease in fluorescence as due to the static quenching, caused by the solvent induced trapping states [35]. A matrix that changes little with temperature will enable one to study molecular properties themselves without changing environmental influence. Poly(methly methacrylate) has been used as such a matrix in many studies [36].

Excitation of ground state dye F to its singlet excited state F^* given:

$$F + h\nu \rightarrow F^*$$

Emission of the fluorescence is the radiative transition of an electronically excited molecule from its singlet excited state to its ground state [10]:

$$F^* \rightarrow F + h\nu'.$$

Fluorescence quenching normally refers to any bimolecular process between the excited singlet state of a fluorescence dye and the second species that enhances the decay rate of the excited state. One can schematically represent the process as:

$$F^* + Q \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (F^*Q)F^*Q$$

where F and F^* represents the fluorescent molecule, and its excited form, Q is the quencher. k_1, k_{-1} and k_2 represent the

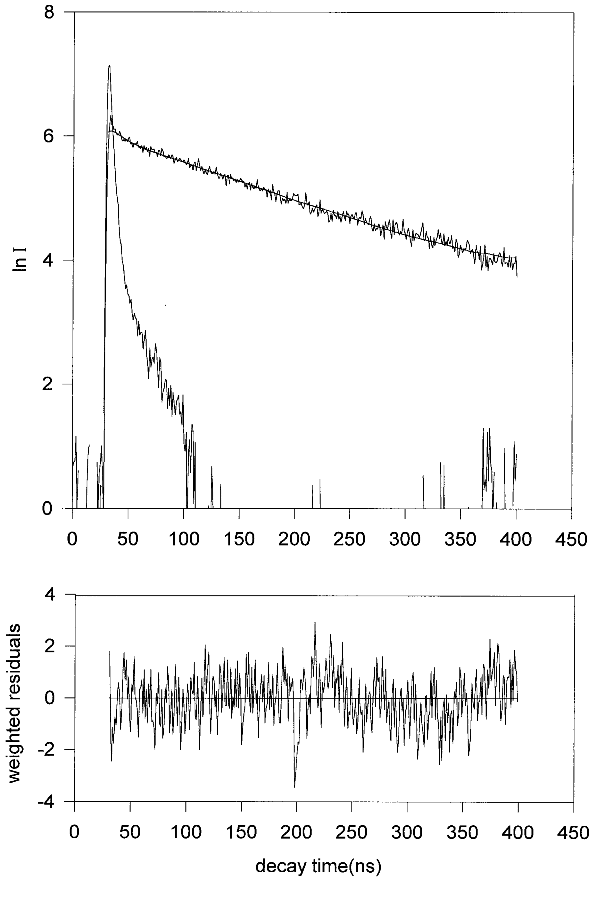

Fig. 1. The fit of the decay curve of P_y according to Eq. (4), at the gelation time, t_g of 200′ at 70°C. The sharp peaked curve present the lamp profile.

diffusional, and internal quenching rate constants respectively. Many types of processes lead to quenching. Kinetically, quenching processes can be divided into two main categories; dynamic and static. In dynamic quenching, diffusion to form an encounter pair (F^*Q) during the excited state lifetime of the dye leads to quenching. In static quenching, diffusion does not occur (and hence is out side of our interest here). Dynamic quenching is most likely to occur in fluid solution, where the dye or quencher is free to move.

Here the quenching efficiency is given by:

$$\gamma = \frac{k_2}{k_{-1} + k_2 + \tau_0^{-1} + k_1[Q]} \tag{1}$$

where τ_0 is the lifetime of F^* where no quenching takes place and $[Q]$ represents the quencher concentration. If

$$k_2 \gg (k_{-1} + \tau_0^{-1} + k_1[Q])$$

then Eq. (1) produces $\gamma \approx 1$ and $k_1 = k_q$ Here k_q is the quenching rate constant and given by Smoluchowski relation [10]. The rate equation for $[F^*]$ with pulse excitation can be written as:

$$\frac{d[F^*]}{dt} = -\tau^{-1}[F^*] + L(t - t')[F] \tag{2}$$

where $[F^*]$ and $[F]$ represents the concentration of F^* and F molecules and $L(t - t')$ is the light pulse of SMS system.

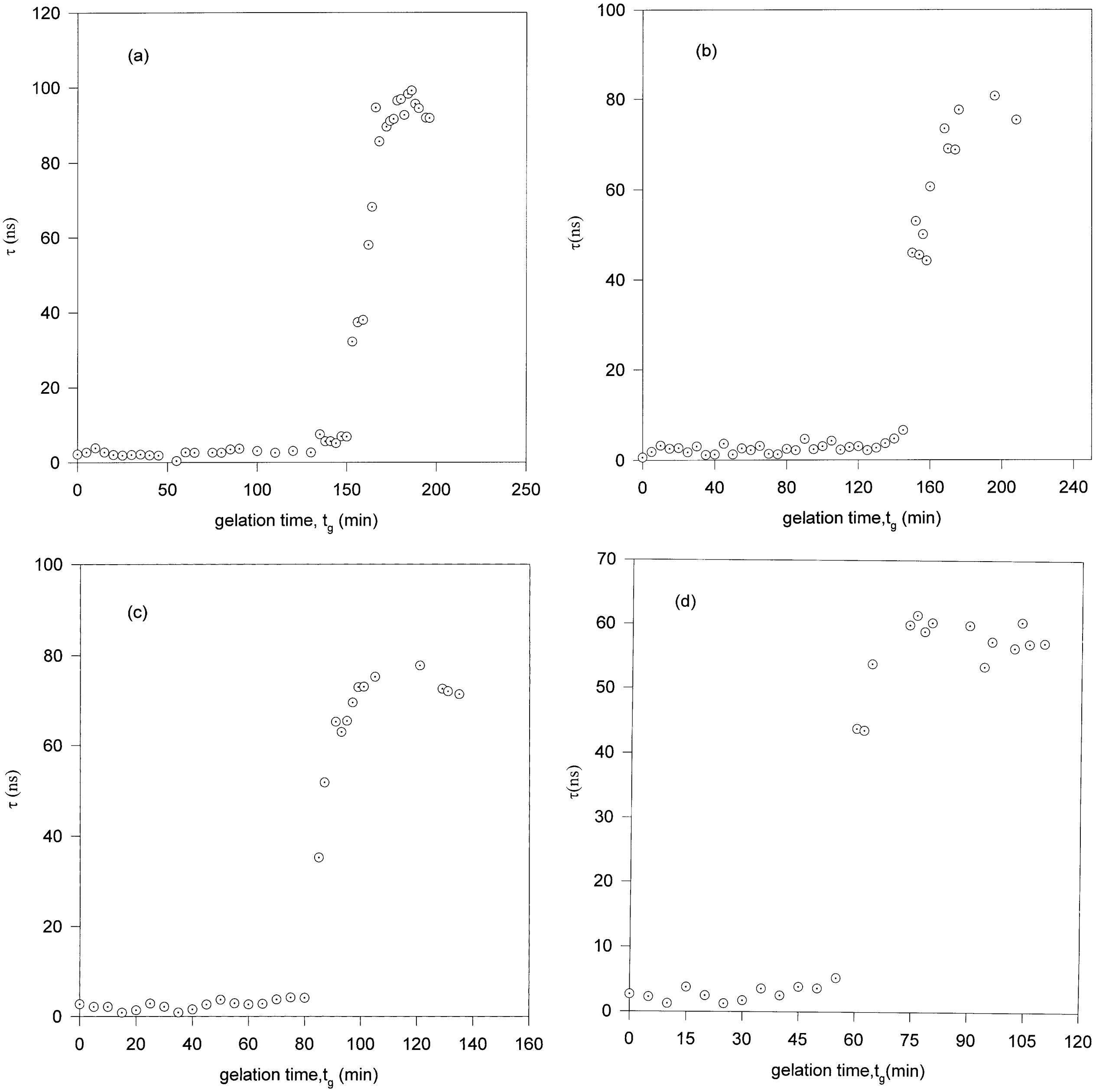

Fig. 2. Plot of the P_y lifetimes, τ versus gelation time, t_g, of (a) 0.025, (b) 0.05, (c) 0.1, (d) 0.2% DVB content samples.

Here τ^{-1} is given by the following relation call Stern-Volmer equation:

$$\tau^{-1} = \tau_0^{-1} + k_q[Q] \quad (3)$$

Solution of Eq. (2) produces the decaying fluorescence intensity as:

$$I(t) = A\exp\left(\frac{t}{\tau}\right) \quad (4)$$

Where A is the preexponential factor. The observed fluorescence decay of a sample, $\phi(t)$is related to the actual fluorescence decay, $I(t)$ and the SMS light pulse by the convolution integral:

$$\phi(t) = \int_0^t L(t-t')I(t')\mathrm{d}t' \quad (5)$$

3. Experimental

3.1. Materials

Styrene (S, Merck) and commercial DVB (DVB, Merck) were shaken with 10% NaOH, washed with water, dried with anhydrous $CaCl_2$, and finally distilled under reduced pressure. Purity was checked by gas chromatography. Various batches of DVB solution were used. Batch analyses ranged between 50 and 60% DVB isomers (m-DVB: p-DVB ratio = 3–3.2: 1), the rest being ethylstyrene. Benzoyl peroxide (BP, Merck) was recrystallized from acetone solution.

3.2. Gelation

The free-radical crosslinking copolymerization (FCC) of S and DVB was performed in bulk in the presence of BP as an initiator. The initiator concentration was held constant at $[I]_0 = 0.100$ M. The reaction mixtures were prepared by dissolving BP in the selected S–DVB monomer mixture and flushing with nitrogen 10 min prior to polymerization. In this work, mainly two sets of FCC experiments were performed; in the first set, different DVB content in the range from 0.025 to 0.20 vol% was used for each FCC experiment at a constant temperature (70°C).

4. Fluorescence measurements

In situ fluorescence decay experiments from which P_y lifetimes can be determined were performed using Photon Technology International's (PTI) Strobe Master System (SMS). In the strobe, or pulse sampling technique [37] the sample is excited with a pulse light source. The name comes about because the PMT is gated or strobed by a voltage pulse that is synchronized with the pulsed light source. The intensity of fluorescence emission is measured in a very narrow time window on each pulse and saved in a computer. The time window is moved after each pulse. The strobe has the effect of turning of the PMT and measuring the emission intensity over a very short time window. When the data has been sampled over the appropriate range of time, a decay curve of fluorescence intensity versus time can be constructed. Because the strobe technique is intensity-dependent, the strobe instrument is much faster than Single Photon Counting (SPC) and even faster than a phase instrument. The strobe instrument is much simpler to use than SPC and data is easier to interpret than with a phase system. Because of these advantages SMS is used to monitor gelation processes which take around few hours.

All lifetime measurements were made at 90° to the incident beam and the slit widths were kept at 10 nm. The gelation experiment was performed in a round quartz cell, which was placed in the SMS, and fluorescence decays were collected over three decades of decay time. The sample was illuminated with 350 nm excitation light and pyrene fluorescence emission was detected at 393 nm. Deconvolution of $I(t)$ from Eq. (5) is performed using iterative non-linear-least-squared fitting technique. The uniqueness of the fit of the data to the model is determined by χ^2 ($\chi^2 < 1.20$), the distribution of weighted residuals, and the autocorrelation of the residuals. All measurements were made at 70°C temperature and sample was deoxygenated by bubbling nitrogen through for 10 min.

5. Results and discussion

In order to monitor gelation processes the fluorescence decay curves were measured and then fitted to Eq. (4). The

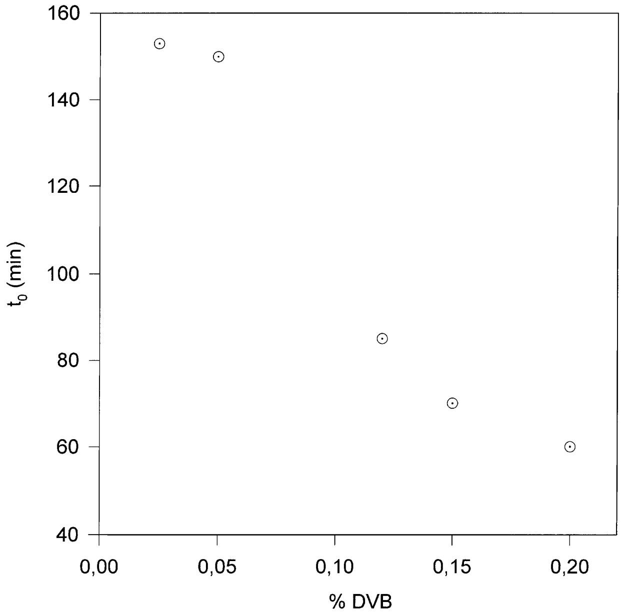

Fig. 3. Plot of the time in the onset of gelation, t_0, versus crosslinker contents.

decay curve and its fit to Eq. (4) are shown in Fig. 1 for the gelation time, t_g of 200 min at 70°C for 0.025% DVB content sample. Here the gelation time, t_g is defined as the elapsed time during gelation process. τ values were produced at each gelation step using non-linear least square analysis. τ values obtained during FCC are plotted versus gelation time, t_g, in Fig. 2(a)–(d) for 0.025, 0.05, 0.1 and 0.2% DVB content samples, respectively. As seen in Fig. 2, Py lifetimes, τ increased drastically from very low values (3 ns) to their unquenched (τ_0) values during gelation at each DVB content sample. The onset of gelation time (t_0) at which sol–gel transition starts, decreased as DVB content is increased, indicating the early gelation process takes place at high DVB content. Fig. 3 represents the plot of t_0 versus DVB. In order to quantify the behaviour of τ versus time, the Stern-Volmer type of quenching mechanism is proposed for the fluorescence decay of P_y during gelation process, where Eq. (3) can be employed and rewritten as follows:

$$\tau^{-1} = \tau_0^{-1} + k_q[S] \qquad (6)$$

Here it is assumed that S is the only quencher for the excited P_y^* molecules, i.e. most of the bimolecular quench-

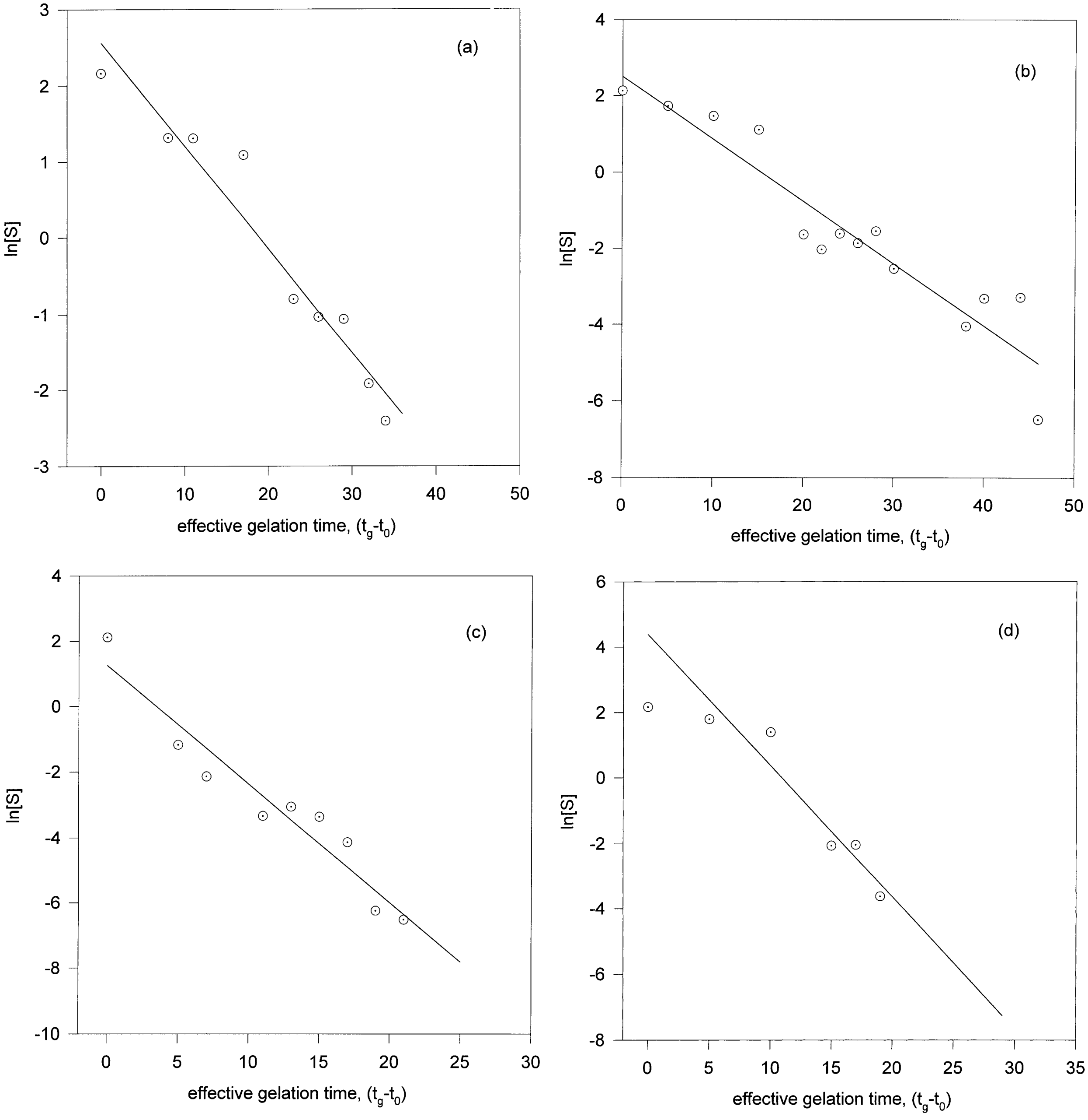

Fig. 4. The fit of the data in Fig. 2 according to Eq. (8), where the effective gelation time, (t_g–t_0) was used. The slope of the linear relations produce the composite rate constants, k_r for the polymerization of S for (a) 0.025, (b) 0.05, (c) 0.1, (d) 0.2% DVB content samples.

ing processes take place between S and P_y^*, because the amount of DVB in the system is negligible compared to S molecules. τ_0 values between 100 and 60 ns, are chosen above $t_g = 180$ and 80 min, where the gelation is completed and the ideal solid network is reached for the corresponding samples. By knowing the $[S_0]$ value as 9.38 M, k_q is measured before the polymerization has started and found to be 4.63×0^7 $M^{-1} s^{-1}$. Using the k_q value and the measured τ values during the gelation process, $[S]$ values are obtained from Eq. (6).

A naive model [38] for quick interpretation of the behaviour of $[S]$ versus gelation time, t_g can be employed, where the first step in free-radical polymerization is the decomposition of the initiator molecule with the rate constant, k_i into two species carrying unpaired electrons called free radicals. A free radical can then react to open the double bond of a vinyl monomer and add to it, with one electron remaining unpaired. In a very short time, usually a few seconds or less, many more monomers add successively to the growing chain with the propagation rate constant, k_p. Finally two radicals react to end each other's growth activity and form one or more polymer molecules. This bimolecular process is called termination reaction and is identified with the rate constant, k_t. During the free-radical crosslinking copolymerization (FCC), addition of divinyl monomers to the growing chain results in the formation of polymer molecules with reactive sites ('pendant vinyl groups'). These reactive sites on polymer chains offer the possibility of forming chemical structures of macroscopic dimensions called polymer gels. The rate of consumption of monomer is usually called the rate of polymerization:

$$\frac{d[S]}{dt} = -k_r[S]. \tag{7}$$

which is applied only under steady-state conditions. Here $[S]$ is the concentration of monomer, (styrene) and k_r is the composite rate constant, which is composed of k_p, k_i and k_t rates [38]. The solution of the Eq. (7) produces the relation for the monomer consumption as follows:

$$[S] = [S_0]\exp(-k_r t) \tag{8}$$

where $[S_0]$ is the concentration of monomer (styrene) at $t = 0$.

The produced $[S]$ consumption curves versus effective gelation time, (t_g-t_0) obey the relation in Eq. (8). Here the effective gelation time (t_g-t_0) is defined as the time at which sol–gel phase transition takes place. The logarithmic form of $[S]$ versus (t_g-t_0) are plotted in Fig. 4(a)–(d) for samples of 0.025, 0.05, 0.1 and 0.2% DVB content where t_0 is the onset of gelation time which corresponds to $[S_0]$ value. In Fig. 4 the slope of the linear relations produce the composite rate constants, k_r according to Eq. (8), for FCC polymerizations during gelation. The plot of k_r versus DVB% is shown in Fig. 5 for all samples. It is observed that, as the DVB content is raised, the composite rate constant increases as expected.

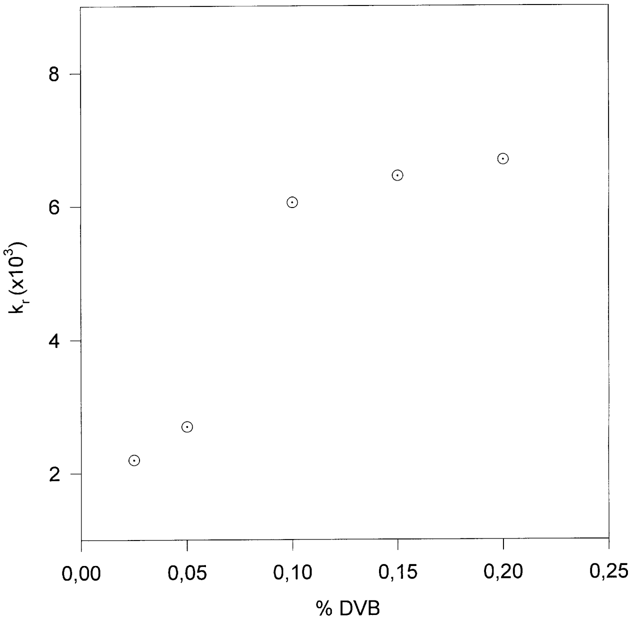

Fig. 5. Plot of k_r versus crosslinker contents.

Here it is interesting to plot the maximum τ values, τ_{max}, versus DVB concentration in Fig. 6 where as DVB is increased τ_{max} decrease. This behaviour of τ_{max} indicates that more unreacted monomers are trapped in the high DVB content samples than low DVB content samples, after the FCC process is completed. However, after afew days, τ_{max} values level off due to polymerization of the left-over monomers. In Fig. 6, solid points represent the τ_{max} values measured after a week from the original FCC

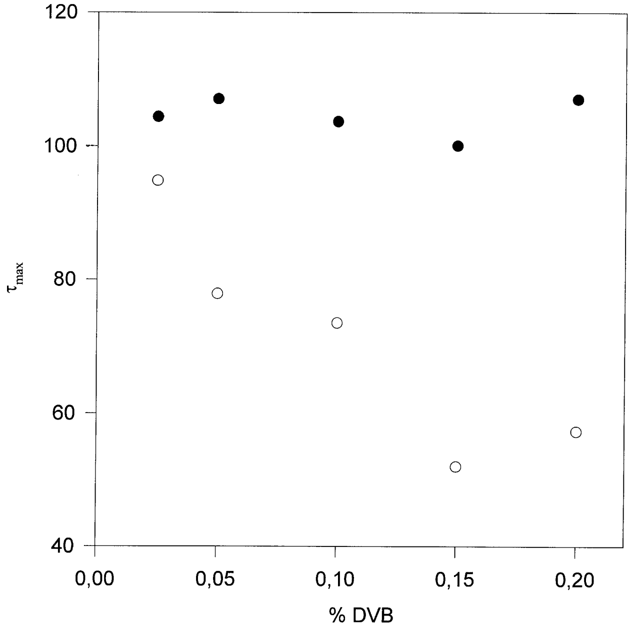

Fig. 6. Plot of τ_{max} obtained in Fig. 2 versus crosslinker contents. Solid points present the τ_{max} data a week after the FCC is completed.

process. Eq. (6) can be used to calculate the amount of unreacted monomer after the FCC process is completed. Here it can be noticed that the similarities between Fig. 3 and Fig. 6, where it is seen that faster polymerization results in having more inreacted monomers trapped in the gel which cause low $\tau_{\max}$ values. However slower polymerization results high $\tau_{\max}$ and less unreacted monomers trapped in the gel.

In conclusion, this work has shown that FTRF technique is quite powerful to understand and to study the FCC process during gelation. Measuring fluorescence lifetimes and modelling them can provide us some useful FCC parameters, which are important to be known.

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