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Fast transient fluorescence technique for monitoring gelation in free-radical crosslinking copolymerization

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Abstract

The fast transient fluorescence technique was used to study the sol–gel phase transition in free-radical crosslinking copolymerization of methyl methacrylate (MMA) and ethylene glycol dimethacrylate. Pyrene (Py) was used as a fluorescence probe for the in situ polymerization experiments. Fluorescence lifetimes of Py from its decay traces were measured and used to monitor the gelation process. Stern–Volmer kinetics was employed to determine the quenching rate constant before the onset of gelation. The MMA consumption rate was measured during the gelation process using the Stern–Volmer model. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Fast transient fluorescence; Sol–gel phase transition; Lifetimes

1. Introduction

In chemical gelation, the molecules crosslink into larger clusters by forming covalent bonds in various ways. In condensation polymerization, a network is formed by polymerizing bifunctional units and the polyfunctional units serve as crosslinkers. Free-radical crosslinking copolymerization (FCC) has also been widely used to synthesize polymer gels. Several theories have been developed in the past 50 years to describe gel formation in FCC, among which percolation theory provides a basis for modelling sol–gel phase transition [1–3]. The percolation models based on simulation in *n*-dimensional space can predict critical exponents or gel fraction, weight-average degree of polymerization, radius of gyration, etc. near the sol–gel phase transition called the critical region. This theory is, however, unrealistic outside this region due to the difficulty of introduction of realistic mobilities. Other types of theories called "mean-field theories" such as the statistical and kinetic theories are based on a "tree approximation". Statistical theories originate from Flory [4] and Stockmayer [5] and assume equal reactivities of functional groups and the absence of cyclization reactions. The critical exponents in percolation theory differ from those found in Flory–Stockmayer. 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 that may suggest a more realistic approach to the mechanism of gelation process [6–9]. Kinetic models have been extensively used to describe the relations among the molecular weights of the polymers and the conversion or reaction time during the crosslinking process. In the classical kinetic theory, the rate constant is proportional to the product of the number of functional groups in each reactant. Modification of the classical kinetic theory by using rate constant that also depend on the structural features of the reactants has been done [10].

When an organic dye absorbs light, it becomes electronically excited, then fluorescence occurs from the lowest excited singlet state and decays over a time scale typically of nanoseconds [11,12]. In addition to unimolecular decay pathways for the deexcitation of the excited state, there are a variety of bimolecular interactions that can lead to deactivation. These are referred to collectively as quenching processes, which enhance the rate of decay of an excited state intensity, *I*. For dilute solutions of dye molecules in isotropic media, exponential decays are common. In more complex systems, deviations are often observed. Fluorescence dyes can be used to study local environments, basically with two types of experiments. When the dye is simply added to the system as a small molecule, the dye is referred to as probe, which is available commercially. As a consequence such experiments are easy to carry out. If one can prepare an experiment that allows the dye to be attached covalently to a specific

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component of a system such as a polymer chain segment, such dyes are referred to as labels. The following question can be raised: does the presence of the dye perturb the system or perturb its own local environments in the system? Electronic perturbations are most common in high dye concentrations that lead to aggregation, such as in crystalline systems where the excitonic order in the system can be affected by a dye. Mixed organic crystals are typical examples of such systems where host excitation can be trapped by a guest molecule, which acts as a trap for the excitons [13,14]. These perturbations are much less likely when a fluorescent dye is incorporated into an amorphous fluid or glassy phase.

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 [15–19]. TRF spectroscopy with direct energy transfer (DET) from a donor to an acceptor dye and quenching of a donor by an acceptor has been used to characterize internal morphologies of composite polymeric materials [20,21]. Quenching besides DET is a general word used to describe any bimolecular process. Quenching usually decreases the emission decay rate of donor dyes. There are many such mechanisms. The most common ones are electron transfer, exciplex and excimer formation, non-emissive self-quenching and heavy atom effect. The most important feature of these quenching mechanisms involves interactions between groups over different interaction distances.

TRF and steady-state fluorescence (SSF) techniques were employed to study isotactic polystyrene in its gel state. A pyrene derivative was used as a fluorescence molecule to monitor the polymerization, ageing 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 the in situ observations of the sol–gel phase transition in free-radical crosslinking copolymerization using the SSF technique [23–29]. The bond percolation model was employed to obtain some critical exponents during the sol–gel transitions of such systems.

In this article, the strobe technique that is named as FTRF was used to study the sol–gel transition in the FCC of MMA and EGDM. The major advantage of the strobe technique over other lifetime instruments is the time duration of a single experiment that takes only seconds. In this work, this advantage of the strobe technique is used to make at least 20–30 lifetime experiments during the gelation of MMA and EGDM, over a time interval of 1 h. In situ FTRF experiments were carried out by illuminating the sample cell during gelation and the fluorescence decay traces were observed using the Strobe Master System (SMS). The Stern–Volmer quenching equation was employed to monitor MMA consumption during the sol–gel phase transition.

2. Theoretical considerations

2.1. Fluorescence quenching

The fluorescence and phosphorescence intensities of aromatic molecules are affected by both radiative and non-radiative processes [30]. 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 approximation [31]. 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 the fluorescence characteristics of pyrene solutions in various solvents and observed that the rate of monomer internal quenching is affected by solvent quality [32]. Weber et al. reported the solvent dependence of energy trapping in phenanthrene block polymers and explained the decrease in fluorescence yield with the static quenching, caused by the solvent induced trapping states [33]. A matrix that changes little with temperature will enable one to study molecular properties themselves without changing environmental influence. Poly(methly methacrylate) (PMMA) has been used as such a matrix in many studies [34].

Emission of the fluorescence is the radiative transition of an electronically excited molecule from its singlet excited state to its ground state [11,12]. 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

$$F^* \xrightarrow{k_f, k_{nr}} F,$$

$$F^* \xrightarrow{k_q[Q]} F$$

where F and F^* represent the fluorescent molecule and its excited form, respectively, Q is the quencher, and k_f, k_{nr} and k_q represent the fluorescence, non-radiative and quenching rate constants, respectively. Many types of processes lead to quenching. Kinetically, the quenching process can be divided into two main categories: dynamic and static. In dynamic quenching, diffusion to form an encounter pair during the excited state lifetime of the dye leads to quenching. In static quenching, diffusion does not occur (which is not of our interest). Dynamic quenching is most likely to occur in fluid solution, where the dye or the quencher is free to move. If the quenching rate can be characterized in terms of a single rate coefficient (k_q) and the unquenched decay rate of F, in terms of a unique lifetime,

τ_0, then the quenching kinetics will follow the Stern–Volmer equation as follows:

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

where [Q] represents the quencher concentration.

2.2. Kinetic model

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 [35]. This bimolecular process is called the 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 the monomer is usually called the rate of polymerization and is given by the following equation:

$$\frac{d[M]}{dt} = -\frac{k_p k_i^{1/2}}{k_t^{1/2}}[M][I]^{1/2} \quad (2)$$

which is applied only under steady-state conditions. Here [M] and [I] are the concentrations of the monomer and the initiator, respectively. Often the rate constant for initiation, k_i, is large and only a small propagation of the initiator breaks down into radicals, which means that [I] stays constant during the polymerization process and Eq. (2) can be written as

$$\frac{d[M]}{dt} = -k_r[M] \quad (3)$$

where k_r is the composite rate constant. The solution of the Eq. (3) produces the relation for the monomer consumption as follows:

$$[M] = [M_0]\exp(-k_r t) \quad (4)$$

where $[M_0]$ is the concentration of monomer at $t = 0$.

3. Experimental

In this work we monitored the gelation in the FCC of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDM) by using the in situ FTRF technique. The radical copolymerization of MMA and EGDM was performed in bulk in the presence of 2,2′-azobisisobutyronitrile (AIBN) as an initiator at 70°C temperature. Py lifetimes were measured to detect the gelation process where MMA act as an energy sink for the excited Py molecules. The PMMA network however provides an ideal, unchanged environment for the excited Py molecules. Naturally, from these experiments one may expect a drastic increase in Py lifetimes during the gelation process.

EGDM has been commonly used as a crosslinker in the synthesis of polymeric networks. Here, for our use, the monomers MMA (Merck) and EGDM (Merck) were freed from the inhibitor by shaking with a 10% aqueous KOH solution, washing with water and drying over sodium sulfate. They were then distilled under reduced pressure over copper chloride. The initiator, AIBN (Merck), was recrystallized twice from methanol. Here EGDM (0.015%) and AIBN (0.26 wt%) was dissolved in MMA and this solution was transferred into a round quartz cell of 10 mm internal diameter for fluorescence decay measurements.

In situ fluorescence decay experiments from which Py lifetimes can be determined were performed using Photon Technology International's (PTI) Strobe Master System (SMS). In the stroboscopic technique [12,36], the sample is excited with a pulsed light source. The intensity of fluorescence emission is measured in a very narrow time window pulse and saved in a computer. This pulse is called a strobe. The strobe is synchronized with the pulse of the light source and moved along the time scale after each pulse. The strobe has the effect of tuning on 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 emission intensity over time can be constructed.

In the time-correlated single photon counting (SPC) technique, the sample is excited with a pulsed light source. The light source, optics and detector are adjusted so that, for a given sample, no more than one photon is detected. When the source is pulsed, a timer is started. When a photon strikes the detector, the time is measured. Over the course of the experiment, the fluorescence decay curve is constructed by measuring the photon events. The accumulation of counts versus time takes more than minutes, even hours.

In a phase shift fluorometer the sample is illuminated with light whose intensity is sinusoidally modulated with a circular modulation frequency. It is known that irrespective of the complexity of the emission (i.e. single, multi or nonexponential) the emission will also be sinusoidal, but will be shifted by a phase angle and demodulated by a factor relative to the excitation. For a single-exponential decay, as is expected for pure fluorophore dyes in a fluid homogeneous environment, the phase shifts and demodulations can be used to calculate the fluorescence lifetime.

Because the strobe technique is intensity-dependent, strobe instruments are much faster than single-photon counting and even faster than phase modulation. The accurate measurements can be made in minutes and even in

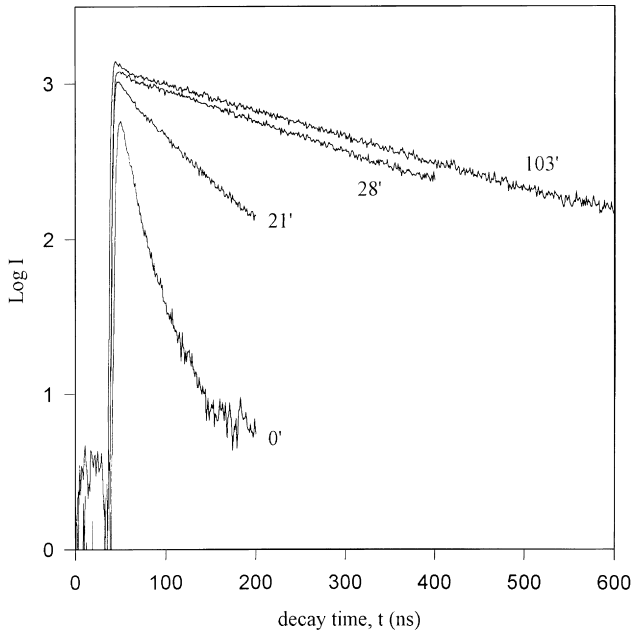

Fig. 1. Fluorescence decay profiles of excited Py, at various gelation steps. I is the Py intensity. Numbers on each curve present the gelation times in minutes.

seconds. Because of these advantages, SMS is used to monitor gelation processes that take about a few hours.

The gelation experiment was performed in a round quartz cell that was placed in the SMS. All lifetime measurements were made at 90° position and the slit widths were kept at 4 nm. Fluorescence decay was collected over three decades of decay time. The sample was then illuminated with

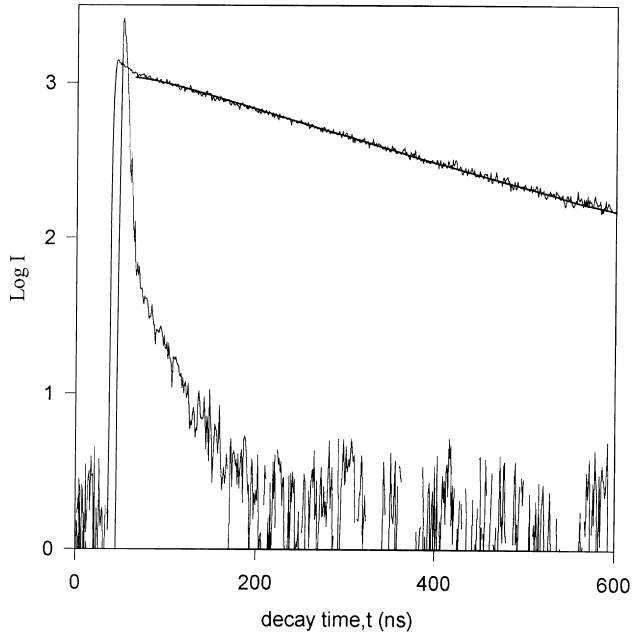

Fig. 2. Fit of the decay curve of Py to Eq. (1), for the gelation of 103 min. The sharp peaked curve is the lamp profile.

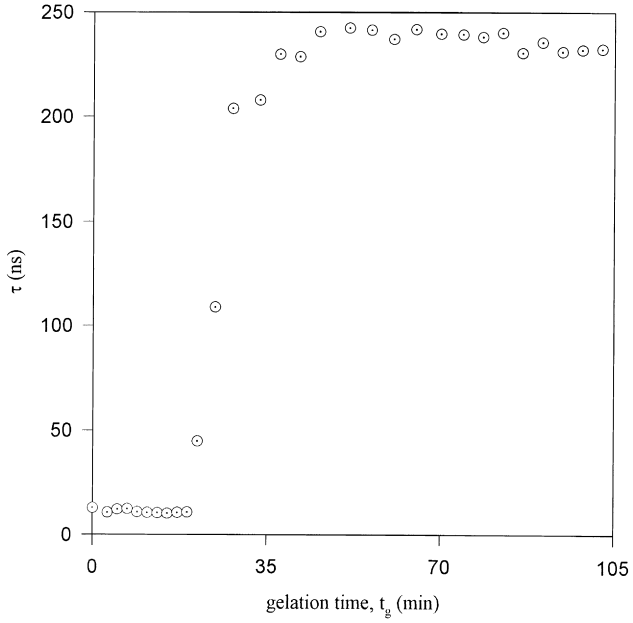

Fig. 3. Plot of lifetimes of Py, τ versus gelation time, t_g.

345 nm excitation light and pyrene fluorescence emission was detected at 395 nm. 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 the sample was deoxygenated by bubbling nitrogen through it for 10 min.

4. Results and discussion

Fig. 1 presents the fluorescence decay profiles of Py at various gelation steps. It is observed that as the gelation time, t_g, is increased, excited pyrenes decay slower and slower by indicating that quenching of excited pyrenes decrease. In order to monitor the gelation processes the fluorescence decay curves are measured and were fitted to the following equation:

$$I = I_0 \exp(-t/\tau) \tag{5}$$

where I and I_0 are the intensities of Py at time t and zero and τ is the lifetime of Py. A typical decay curve and its fit to Eq. (5) is shown in Fig. 2. τ values were produced at each gelation step using the linear least-squares analysis and are plotted versus t_g in Fig. 3. In order to quantify these results a Stern–Volmer type of quenching mechanism is proposed for the fluorescence decay of Py during the gelation process, where Eq. (1) can be employed and rewritten as follows:

$$\tau^{-1} = \tau_0^{-1} + k_q[\mathrm{MMA}]. \tag{6}$$

Here it is assumed that MMA is the only quencher for the excited Py molecules. τ_0 was taken as 200 ns at t_g of 80 min,

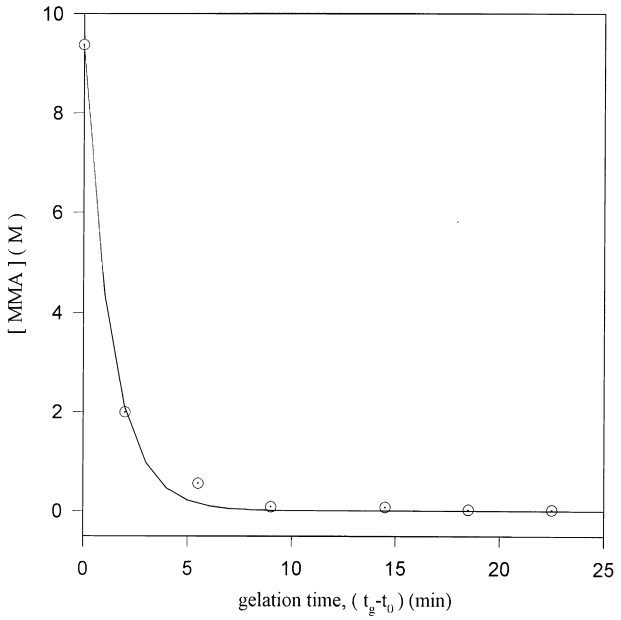

Fig. 4. Plot of the monomer [MMA] consumption versus $(t_g - t_0)$ during gelation, where $t_0 = 20$ min is the time for the onset of gelation.

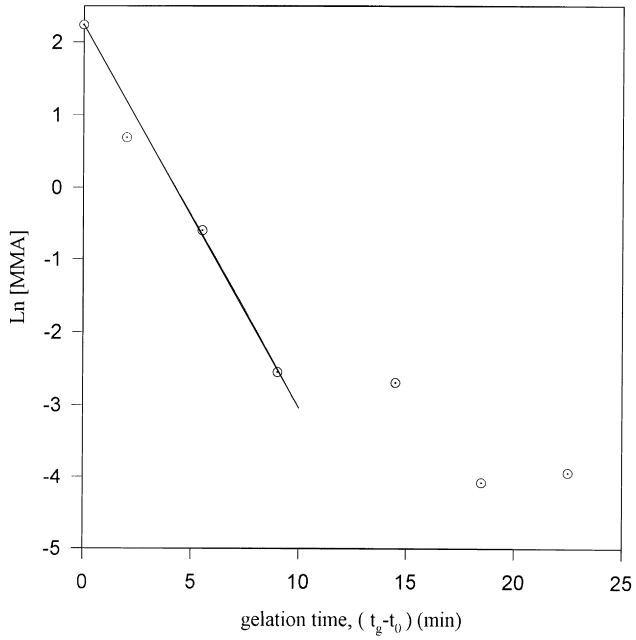

Fig. 5. The fit of the data in Fig. 4 to Eq. (4). The slope of the linear relation produced the composite rate constant, k_r, for the polymerization of MMA.

where the gelation is completed and the ideal solid network is reached. k_q was measured before the polymerization is started and found to be 9.14×10^6 M^{-1} s^{-1}, where the $[MMA_0]$ value was taken as 9.4 M. Using the k_q value and the measured τ values, the [MMA] values are obtained from Eq. (6) and plotted versus $(t_g - t_0)$ in Fig. 4, where t_0 (20 min) was chosen as the onset of gelation time which corresponds to the $[MMA_0]$ value. As seen in Fig. 4 the consumption curve of [MMA] obeys the exponential relation in Eq. (4). The fit of the data in Fig. 4 to Eq. (4) is given in Fig. 5, where the slope of the linear relation produced the composite rate constant, k_r, as 9×10^{-3} s^{-1} for the polymerization during gelation.

The quenching rate constant, k_q, which is found to be 9.14×10^6 M^{-1} s^{-1}, is given in the Smoluchowski model [11], where the magnitude of k_q is related to the diffusion coefficient of the interacting species:

$$k_q = \frac{4\pi N D_m R}{1000} \tag{7}$$

where D_m is the mutual diffusion coefficient, N is Avogadro's number and R the sum of the interaction radii. D_m was calculated from Eq. (7) using the experimentally measured k_q and was found to be 1.7×10^{-5} cm^2 s^{-1}, where R is taken as 7.15 Å. The observed D_m is typical for a small molecule, diffusing in a liquid environment [15,16].

5. Conclusions

This paper introduces a novel method that uses the FTRF technique to measure lifetimes τ of Py during the gelation process where the τ values were used to monitor the monomer consumption. The composite rate constant, k_r, for polymerization during the gelation was measured. Here one has to notice that since we measured lifetimes, no environmental corrections to the data, which are quite problematic when one uses flourescence intensity data from steady state spectrometers, are needed. In the future we are planning to measure the composite rate constants at various temperatures which can be used to produce the activation energy for monomer consumption. Besides that the fractal dimension of a gel at the critical point can be obtained using the FTRF technique where the DET method can be applied between the donor and acceptor dyes. Studying the fractal behaviour of a network at the gel point may help one to understand the percolation model during gelation.

References

[1] Stauffer D. Introduction to percolation theory. London: Taylor & Francis, 1985.
[2] Stauffer D, Coniglio A, Adam M. Adv Polym Sci 1982;44:103.
[3] Herrmann H. J Phys Rev 1986;153:136.
[4] Flory PJ. J Am Chem Soc 1941;63:3083.
[5] Stockmayer WH. J Chem Phys 1943;11:45.
[6] Mikos AG, Takoudis CG, Peppas NA. Macromolecules 1986; 19:2174.
[7] Tobita H, Hamielec AE. Macromolecules 1989;22:3098.
[8] Batch GL, Macosko CW. J Appl Polym Sci 1992;44:1711.
[9] Okay O. Polymer 1994;35:796.
[10] Dusek K. J Macromol Sci—Chem 1991;A28:843.
[11] Birks JB. Photophysics of aromatic molecule. New York: Wiley-Interscience, 1971.
[12] Lakowicz JR. Principles of fluorescence spectroscopy. New York: Plenum, 1983.
[13] Pekcan Ö. Mol Phys 1979;38:1233.

[14] Pekcan Ö. Solid State Phys 1981;14:745.
[15] Pekcan Ö, Winnik MA, Croucher MD. Macromolecules 1983;16:699.
[16] Pekcan Ö, Winnik MA, Croucher MD. J Polym Sci Polym Lett 1983;21:1011.
[17] Pekcan Ö, Winnik MA, Croucher MD. Phys Rev Lett 1988;61:641.
[18] Pekcan Ö, Egan LS, Winnik MA, Croucher MD. Macromolecules 1990;23:2210.
[19] Pekcan Ö. Chem Phys Lett 1992;20:198.
[20] Winnik MA. In: Feast J, Munro H, editors. Polymer surfaces and interfaces, London: Wiley, 1983 (chap. 1).
[21] Winnik MA, Pekcan Ö, Chen L, Croucher MD. Macromolecules 1988;21:55.
[22] Panxviel JC, Dunn B, Zink JJ. J Phys Chem 1994;93:2134.
[23] Pekcan Ö, Yilmaz Y, Okay O. Chem Phys Lett 1994;229:537.
[24] Yilmaz Y, Pekcan Ö, Okay O. Polymer 1996;37:2049.
[25] Pekcan Ö, Yilmaz Y, Okay O. J Appl Polym Sci 1996;61:2279.
[26] Pekcan Ö, Yilmaz Y. Progr Coll Polym Sci 1996;102:89.
[27] Pekcan Ö, Yilmaz Y, Okay O. Polymer 1997;38:1693.
[28] Yilmaz Y, Erzan A, Pekcan Ö. Phys Rev E 1998;58:7487.
[29] Okay O, Kaya D, Pekcan Ö. Polymer 1998;40:6179–87.
[30] Kropp LJ, Dawson RW. Fluorescence and phosphorescence of aromatic hydrocarbons in polymethylmethacrylate. In: Lim EC, editor. International Conference on Molecular Luminescence, New York, 1969.
[31] Bixon M, Jortner J. J Chem Phys 1968;48:715.
[32] Birks JB, Lumb MD, Munro IH. Proc R Soc A 1964;277:289.
[33] Kamioka K, Weber SE, Morishima Y. Macromolecules 1988;21:972.
[34] Jones PF. Siegel. J Chem Phys 1964;50:1134.
[35] Young RJ. Introduction to polymers. New York: Chapman & Hall, 1983.
[36] Ware WR, James DR, Siemiarczuk A. Rev Sci Instrum 1992;63:1710.