ELSEVIER

Polymer 42 (2001) 6425–6430

polymer

www.elsevier.nl/locate/polymer

EPR study of the radical polymerization of 3-[tris(trimethylsilyloxy)silyl]propyl methacrylate

N. García[a], J. Guzmán[a,*], E. Riande[a], P. Calle[b], C. Sieiro[b]

[a]*Instituto de Polímeros, CSIC, Juan de la Cierva, 3, 28006-Madrid, Spain*
[b]*Departamento de Química Física Aplicada, Universidad Autónoma de Madrid, 28049-Madrid, Spain*

Received 22 January 2001; received in revised form 10 February 2001; accepted 26 February 2001

Abstract

The kinetics of the radical polymerization of 3-[tris(trimethylsilyloxy)silyl]propyl methacrylate was studied in benzene and dioxane/hexane solutions at different conditions of temperature, monomer and initiator concentrations by using ultraviolet and electron paramagnetic resonance spectroscopic techniques. The values of the ratios between the propagation rate constant and the square root of the termination rate constant ($k_p/k_t^{1/2}$) were determined by UV spectroscopy by measuring the changes of absorbance with time at several wavelengths in the range 275–285 nm, where appropriate changes in absorbance were observed. The values of $k_p/k_t^{1/2}$, in the temperature interval 50–70°C, lie in the range 0.40–0.53 $\mathrm{l}^{-1/2}\mathrm{mol}^{-1/2}\mathrm{s}^{-1/2}$. Measurements of the radical concentrations, the efficiency factor of the initiator and of the absolute rate constants k_p and k_t were carried out using electron paramagnetic resonance techniques. The values of k_p are in the range 500–1000 $\mathrm{l\,mol}^{-1}\,\mathrm{s}^{-1}$ in the temperature interval 50–70°C, in fair agreement with those extrapolated from results obtained by pulsed-laser/size-exclusion chromatography at lower temperatures. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Radical polymerization; Unsaturated monomers containing silicon; Kinetic constants

1. Introduction

The determination of propagation and termination rate constants in the radical polymerization of unsaturated monomers is an important research field in polymer science. Acrylic and methacrylic polymers constitute one of the most important polymer families due to the high possibility that the ester residue presents to synthesize monomers with a varied set of chemical structures. Among the diversity of applications of the polymethacrylates, their use as raw materials for the preparation of contact lenses stands out [1]. By copolymerization of hydrophilic methacrylic monomers, such as hydroxyalkyl methacrylates, with a monomer of high content in silicon, materials with high permeability to oxygen are obtained. 3-[tris(trimethylsilyloxy)silyl]propyl methacrylate (TRIS) is a monomer that, given its high content in silicon, shows these characteristics [2–4] and therefore the study of kinetic parameters that govern its radical polymerization is of interest.

Very recently, Muratore et al. [4] have determined the propagation rate constants of TRIS by pulsed-laser polymerisation/size-exclusion chromatography (PLP/SEC). Electron paramagnetic resonance spectroscopy (EPR) is also an important tool to study kinetics of radical polymerization because the propagating free radicals concentration can be directly determined in real time. Usually the EPR experimental values of the propagation rate constants k_p are in poor agreement with those obtained from PLP/SEC [5,6], making it very important to derive values independent of the measurement method. The main shortcomings in the study of radical polymerizations by EPR spectroscopy arise from the very low radical concentrations ($<10^{-6}$ $\mathrm{mol\,l}^{-1}$) that give rise to low quality EPR signals. The integration of these not well-defined signals sometimes precludes an accurate determination of the radicals' concentrations [7].

In this work, we study by EPR and Ultraviolet spectroscopy the radical polymerization of TRIS to determine the propagation (k_p) and termination (k_t) rate constants, and to compare the results with those obtained by others [4] by PLP/SEC technique.

2. Experimental

2.1. Polymerization reactions and characterization of the polymer

The polymerization reactions of TRIS were carried out at

---

* Corresponding author. Fax: +34-91-564-4853.
E-mail address: jguzman@ictp.csic.es (J. Guzmán).

PII: S0032-3861(01)00169-0

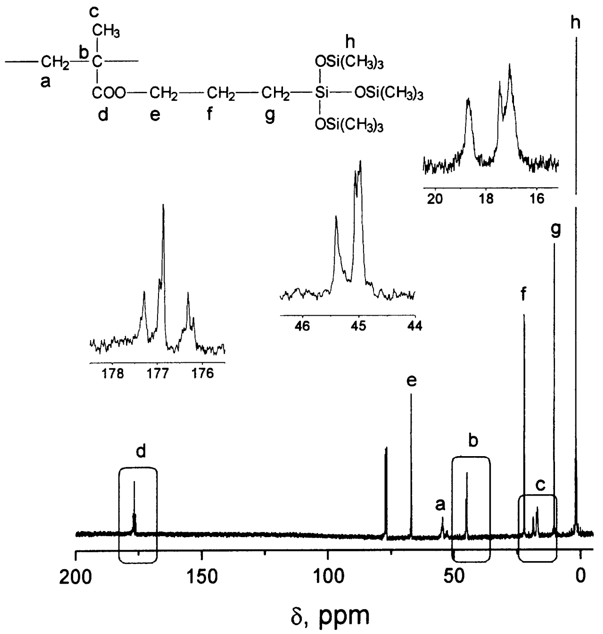

Fig. 1. ^{13}C NMR spectrum of poly{3-[tris(trimethylsilyloxy)silyl]propyl methacrylate} (PTRIS).

temperatures between 50 and 70°C, in benzene and dioxane/hexane solutions with monomer concentrations in the range of 1 mol l^{-1} up to bulk polymerization. 2,2'-Azobisisobutyronitrile (AIBN) was used as initiator at different concentrations between 0.05 and 0.15 mol l^{-1}.The polymer was isolated from the reaction medium by several precipitations in acetone and, finally, dried in high vacuum at room temperature for three days. The characterization of the polymer was made by ^{1}H and ^{13}C NMR spectroscopy, using a Varian XL 300 spectrometer and deuterated chloroform as solvent. The ^{13}C spectrum of poly{3-[tris(trimethylsilyloxy)silyl]propyl methacrylate} (PTRIS) with the corresponding assignment of the resonance signals is shown in Fig. 1. The splitting into well-resolved peaks in the resonance of quaternary carbons of the main chain, the α CH3 and the C=O carbon of the polymer is observed. Three resonance signals appear for each carbon, except for the C=O that presents greater sensitivity to the stereochemical configuration. Following classical assignment in other methacrylic polymers [8], the resonance signals were attributed to different tactic triads and pentads (in the case of the carbonylic carbon), from which the molar fractions of different configurations were calculated. An average molar fraction of syndiotactic dyads of 0.80 ± 0.03 was obtained for PTRIS, and its comparison with the values of the triads and pentads units indicate Bernoullian stereochemical control [9]. The predominance of syndiotactic sequences over isotactic is similar to that found for other methacrylic polymers [10].

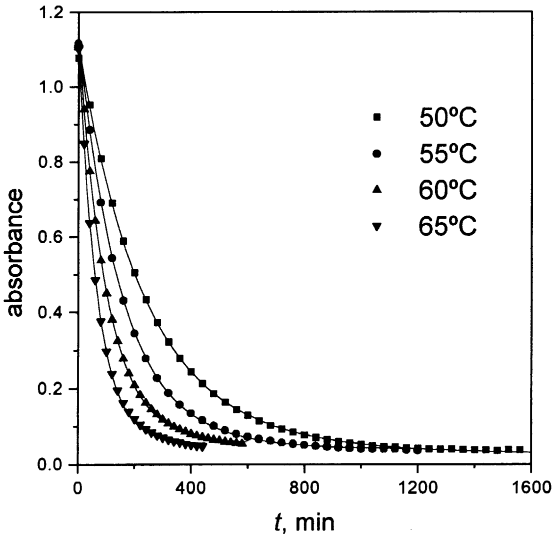

Fig. 2. Changes in the absorbance with the time at 281 nm for the radical polymerization of 3-[tris(trimethylsilyloxy)silyl]propyl methacrylate (TRIS). The continuous lines correspond to the simulated values according to Eq. (1).

The glass transition temperature (T_g) of PTRIS was determined with a Perkin–Elmer DSC8 calorimeter at a heating rate of 10°C/min. The value of T_g, taken at the onset of the separation of the endotherm from the baseline was about 0°C, much lower than the usual values corresponding to other polymethacrylates.

2.2. Radical concentrations measurements

The concentrations of the radical species in the polymerization reactions were determined by electron paramagnetic resonance. EPR spectra were recorded in 3 mm diameter EPR tubes using a Bruker ESP 300 spectrometer. The conditions to register the spectra were microwave frequency, 9.5 GHz; modulation frequency, 100 kHz; modulation amplitude, 3 G; conversion time, 40 ms; time constant, 655 ms; sweep time, 42 s; power, 6.32 mW; receiver gain 3×10^5; scan number, 5.

3. Results and discussion

3.1. Kinetics of polymerization by UV spectroscopy

The kinetics of polymerization were followed by measuring the variation of the monomer concentrations by UV spectroscopy, using a Varian Cary3-Bio UV–Visible spectrophotometer with temperature controlled at ±0.05°C. Values of the absorbances in the region between 275–285 nm were chosen as characteristic absorption wavelengths corresponding to the monomer. In this region, the initiator absorbance is not noticeable. Previous to the experiments, the fulfilment of the Lambert–Beer law was proved in the range of monomer and polymer concentrations at the wavelengths used.

The analysis of the experimental data obtained by UV

Table 1
Experimental values at several temperatures of the ratio $k_p/k_t^{1/2}$, propagation (k_p) and termination rate constants (k_t) in the polymerization of TRIS $[M] = 1$ mol l^{-1} (the values of $k_p/k_t^{1/2}$ were calculated by considering $f = 0.6$. The data are average values of at least five experiments)

T (°C)	$k_p/k_t^{1/2}$	k_p (l mol^{-1} s^{-1})	$k_t \times 10^6$ (l mol^{-1} s^{-1})
70	0.52_6	1025	3.80
65	0.49_6	857	2.98
60	0.46_9	776	2.74
55	0.43_7	639	2.14
50	0.40_8	585	2.06

spectroscopy was made by using the equation [11]:

$$A = A_\infty + (A_0 - A_\infty)\exp\{-2k_p(2fI_0/k_t k_d)^{1/2}[1 - \exp(-k_d t/2)]\}, \quad (1)$$

where k_d, k_p and k_t are the rate constants for initiator decomposition, propagation and termination reactions, respectively, $[M]$ the instantaneous concentration of monomer, $[I_o]$ the initial concentration of initiator, and f is the efficiency of the initiator. A_o, A and A_∞ are, respectively, the absorbances of the monomer at the wavelength considered at the start of the reaction, at time t and at infinite time. Computer simulation of the experimental data of absorbance according to Eq. (1) permits the determination of A_∞ and $fk_p/k_t^{1/2}$. The values of k_d for the calculations at each temperature of interest were taken from the literature [12–15]. The good fit of the simulations to the experimental results, shown in the examples of Fig. 2, indicates that the polymerizations are well described by normal kinetics up to very high conversions at the low monomer concentration levels used in the experiments. The experimental polymerization rate parameter $k_p/k_t^{1/2}$ obtained in the polymerization of TRIS at different temperatures are shown in the second column of Table 1.

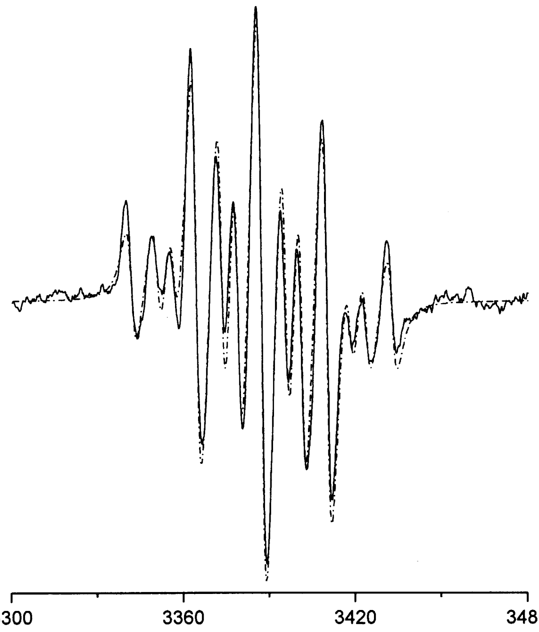

Fig. 3. EPR spectrum of the propagating radicals corresponding to polymerization of 3-[tris(trimethylsilyloxy)silyl]propyl methacrylate at 60°C in benzene solution ($[M_0] = 1$ mol l^{-1}, [AIBN] = 0.1 mol l^{-1}) The simulation of the spectrum is plotted in dash line.

These values certainly characterize the reactivity of a monomer, but it is obvious that a more complete analysis requires the determination of the absolute values of k_p and k_t because the higher (lower) reactivity of a monomer in comparison to others may be due to higher (lower) k_p or lower (higher) k_t. The absolute rate constants of these polymerizations were measured in order to establish the true influence of the chemical structure on the propagation and termination reactions.

3.2. Propagation and termination rate constants

There are several reliable methods to measure the propagation rate constants in free radical polymerization, from the traditional rotating sector [16–22] to the modern pulsed-laser polymerisation/size-exclusion chromatography [5,23–28]. Values of k_p and k_t can also be obtained by measuring the stationary concentration of free radicals by EPR spectroscopy [29,30] that, under certain conditions, is also appropriate to obtain reliable values of the kinetic constants. We have used this technique to study the polymerization of TRIS. In Fig. 3, the EPR spectrum of the propagating radicals corresponding to the 1 M polymerization of TRIS with 0.1 M initiator at 60°C in benzene solution is shown. It can be seen that a typical 13-lines spectrum characteristic of the methacrylic radicals was obtained, with a very good resolution of the resonance signals. Using different reaction conditions and reaction times, similar spectra were observed, without changes in their appearance even at very high conversions, except as it will be seen below for the bulk polymerization. This behaviour shows that there are no changes in the nature of the propagating species during the reaction for low monomer concentrations. The nature of the propagating species in the polymerization of methacrylic monomers, especially methyl methacrylate, has been intensively studied for decades. Tonge et al. [31] showed recently that the EPR spectra of poly(methyl methacrylate) radicals observed under different polymerization conditions can be rationalized by considering only a single free radical even in the case in which the spectrum changes from 13 lines to a 9 lines pattern. In this last case, the spectrum can be adequately simulated by considering two rotamers species of the same radical with two different hyperfine coupling constants for the methylene protons corresponding to each rotamer and one coupling constant for the methyl protons. The normal 13-lines at low conversions requires for the simulation only two hyperfine couplings for the methylene protons of the radical and one for the corresponding methyl protons. It is possible to simulate the spectra corresponding to our radicals by taking

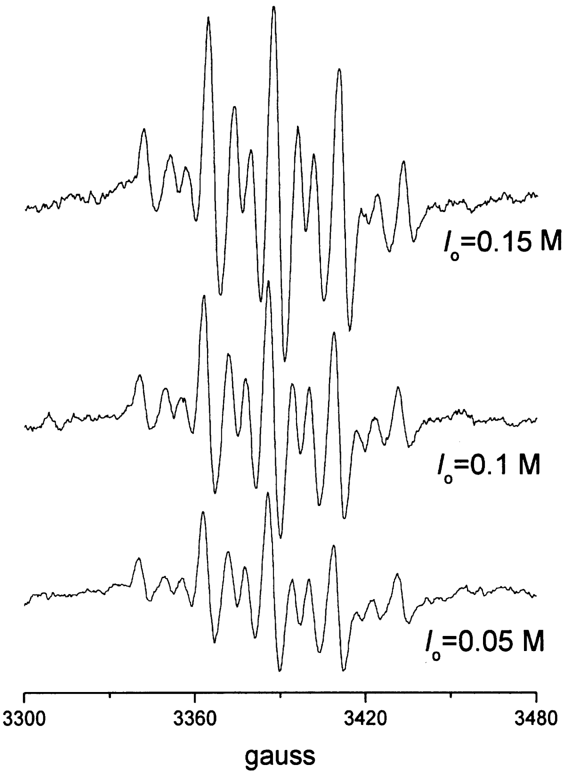

Fig. 4. Variation of the EPR spectrum in the polymerization of 3-[tris(trimethylsilyloxy)silyl]propyl methacrylate at 60°C as a function of the initiator concentration.

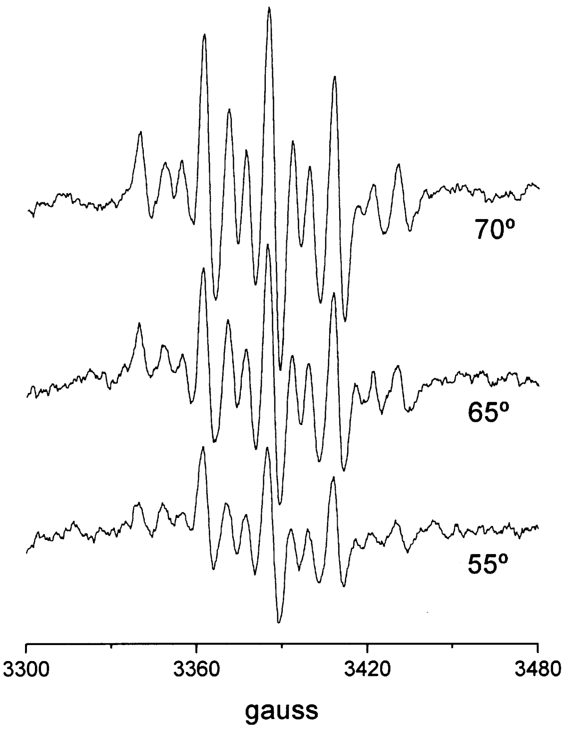

Fig. 5. Variation with temperature of the EPR spectrum in the polymerization of 3-[tris(trimethylsilyloxy)silyl]propyl methacrylate.

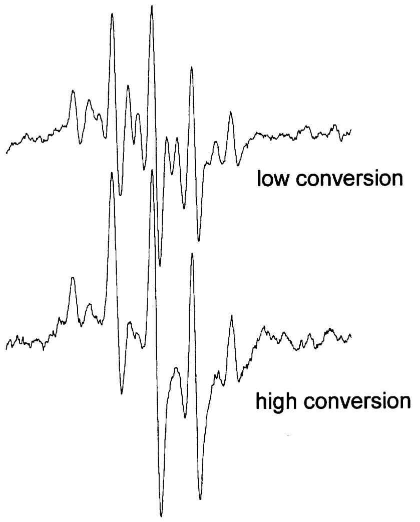

Fig. 6. Changes in the spectrum pattern depending on the conversion for the bulk polymerization of 3-[tris(trimethylsilyloxy)silyl]propyl methacrylate at 70°C.

into account these considerations and the results of the simulation are also shown in Fig. 3. The best hyperfine couplings necessary to the simulation were 22.45 for the methyl protons and 14.1 and 8.6 G for each proton of the methylene group, values very similar to those indicated by Tonge et al. [31] for the radicals corresponding to the polymerization of methyl methacrylate at low conversions.

The influence of the concentration of initiator on the polymer radical concentration is shown in Fig. 4, where the increase in the intensity of the spectral signals is clearly observed. The double integral corresponding to the different spectra represented against the squared root of the concentrations of initiator give a straight line, indicating that the polymerizations follow the normal kinetic mechanism of radical polymerizations at relatively high AIBN concentrations. On the other hand, the influence of temperature on the radical concentration is shown in Fig. 5, where it can be seen the intensity increase of the spectral signals with temperature. This behaviour is due to a more important contribution to the formation of free radicals by the increase in k_d than that of destruction as consequence of the corresponding increase in k_t.

In the bulk EPR experiments at high conversions, the 9-lines spectrum is scarcely observed during the reaction and only at the end of the polymerization the change of 13 to 9 lines is clearly detected (Fig. 6). This indicates that the mobility of the radicals is slightly affected by the changes occurring in the viscosity of the medium during the polymerization, in contrast to that occurs in the polymerization of MMA where the change from 13 to 9 lines in the EPR spectra of the polymerization system [30,31] is observed at relatively low conversions. This fact proves the non-existence of the Norrish-Trommsdorf [32,33] effect in the polymerization of TRIS, which we had already supposed in view of UV spectroscopy measurements.

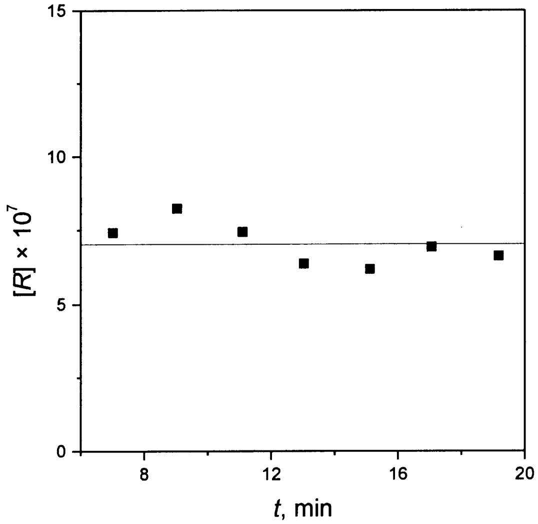

Fig. 7. Time dependence of the radical concentrations for the bulk polymerization of 3-[tris(trimethylsilyloxy)silyl]propyl methacrylate at 70°C ([AIBN] = 0.077 mol l^{-1}).

The double integration of the signals corresponding to different spectra taken at several reaction times and their comparison with the EPR spectrum of 2,2,6,6-tetramethyl-4-hydroxylpiperidine-1-oxyl (TEMPOL), used as standard, permits to obtain the radical concentrations. As shown in Fig. 7, the changes with time of the stationary radical concentration are negligible, indicating that the possible effects of viscosity on the rate constants are not appreciable, at least at the initiator concentrations used in our experiments.

The values of k_p may be directly obtained from the equation

$$-\frac{d[M]}{dt} = k_p[R][M], \tag{2}$$

where $[R]$ is the radical concentration. Integration of this equation yields

$$\ln\frac{[M_0]}{[M]} = k_p \int_0^t [R]\, dt. \tag{3}$$

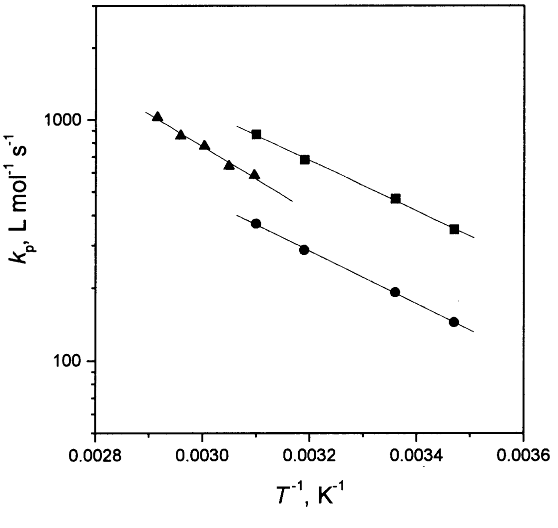

Fig. 8. Arrhenius plot of the k_p values in the polymerization of 3-[tris(trimethylsilyloxy)silyl]propyl methacrylate. Our results (▲) are compared with those obtained by Muratore [4] with different calibration standards (■ standard PTRIS; ● standard PMMA).

By taking into account that the steady state radical concentration remains practically constant with time, the value of k_p is easily obtained from the slope of the straight line corresponding to the integrated equation. The values thus determined at different temperatures are shown in column 3 of Table 1. No significant differences were found in the values of the propagation and termination rate constants obtained with monomer concentrations about 1 mol $l^{-1}$and changing the initiator concentration from 0.05 to 0.15 mol l^{-1}. The errors involved in the determination of k_p were about 15%. On the other hand, these values of k_p in dilute solution are slightly below than those obtained in bulk, although these deviations are within the experimental accuracy.

The radical disappearance rate is given by the expression

$$-\frac{d[R]}{dt} = 2fk_d[I] - k_t[R]^2. \tag{4}$$

In the stationary state, the left-hand side of this equation is zero. Therefore, in order to calculate the absolute values of the termination rate constants it is necessary to determine the true value of the efficiency factor, f. Values of f can be determined by trapping of the radicals by means of a stable radical such as TEMPOL, and measuring its time concentration decay. However, we have found some problems in the determination of f with this method, because straight lines are not obtained in the graphs of the concentration of TEMPOL vs. time. Therefore, at this moment we prefer to consider for f an approximate value of 0.6, as it is habitually observed in the polymerizations of similar monomers. The values thus calculated for k_t are shown in the last column of Table 1.

It is well known that there are usually significant differences in the magnitude of the reported values of k_p, depending on the measuring technique and it is very important to arrive to an adequate concordance among the values of the polymerization parameters. The EPR spectroscopic techniques have been reported to give results three times lower than those determined by pulsed-laser polymerization [5,6] and it is normally accepted that an adequate comparison between experimental values is only possible if the same measuring technique is used. However, this does not seem to be the case for TRIS. In Fig. 8, the temperature dependence of k_p for the polymerization of TRIS is shown. Here the values of k_p determined by Muratore et al. [4], at temperatures between 25 and 50°C, are also included. As can be seen, the values of k_p obtained with both techniques (PLP/SEC and EPR) for the bulk polymerization of TRIS seem to be in fair agreement in the temperature interval from 25 to 75°C. This non-habitual agreement is presumably due to the good resolution of the EPR spectra of the poly{3-[tris(trimethylsilyloxy)silyl]propyl methacrylate} radicals that permit their adequate double integration. Nevertheless it is noteworthy to indicate that also large errors may occur with PLP/SEC procedures [34] depending on the calibration methods as Muratore et al. [4] have indicated and shown in Fig. 8.

The values of the Arrhenius parameters were found to be 9.2×10^6 l mol^{-1} s^{-1} for A and 26.1 kJ mol^{-1} for the activation energy E_a in relatively fair agreement with those reported for the polymerization of several methacrylates [34], including the reported results of Muratore et al. [4] for the polymerization of TRIS. Therefore, we consider that the results of EPR shown in this work seem to indicate that it is possible to obtain similar k_p values in radical polymerization using different measuring techniques.

Acknowledgements

This work was supported by the CICYT (Comisión Interministerial de Ciencia y Tecnología) through the Grant MAT99-1127-C04-01.

References

[1] Mack EF, Okano T, Kim SW. In: Peppas NA, editor. Hydrogels in medicine and pharmacy, Vol. II. Boca Raton, FL: CRC Press, 1987.
[2] Künzler JF, McGee JA. Contact lens materials. Chem Ind 1995;August:1.
[3] Muratore LM, Heuts JPA, Davis TP. Macromol Chem Phys 2000;201:985–94.
[4] Muratore LM, Coote ML, Davis TP. Polymer 2000;41:1441–7.
[5] Hutchinson RA, Beuermann S, Paquet Jr DA, McMinn JH, Jackson C. Macromolecules 1998;31:1542–7.
[6] Matsumoto A, Mizuta K, Otsu T. J Polym Sci, Part A: Polym Chem 1993;31:2531–9.
[7] Buback M, Gilbert RG, Russell GT, Hill DJT, Moad G, O'Driscoll KF, Shen J, Winnik MA. J Polym Sci, Part A: Polym Chem 1992;30:851–63.
[8] Pham QT, Petiaud-Hugues Waton R, Llauro MF. Proton and carbon NMR spectra of polymers, vol. 3. Chichester: Wiley, 1984.
[9] Koenig JL. Chemical microstructure of polymer chains. New York: Wiley, 1980. p. 328.
[10] Matsumoto A, Mizuta K, Otsu T. Macromolecules 1993;26:1659–65.
[11] García N, Guzmán J, Riande E, García F, de la Peña JL, Calle P, Jimeno ML. J Polym Sci, Part A: Polym Chem 2000;38(21):3855–63.
[12] Tulig TJ, Tirrel M. Macromolecules 1982;15:459–63.
[13] Bawn CEH, Verdin D. Trans Faraday Soc 1960;56:815–22.
[14] van Hook JP, Tobolsky AV. J Am Chem Soc 1958;80:779–82.
[15] McKenna TF, Villanueva A, Santos AM. J Polym Sci, Part A: Polym Chem 1999;37:571–88.
[16] Moad G, Solomon DH. The chemistry of free radical polymerization. Oxford, UK: Pergamon Press, 1995.
[17] Olaj OF, Kornherr A, Zifferer G. Macromolecules 1999;32:8800–6.
[18] Bamford CH, Barb WG, Jenkins A, Onyon PF. The kinetics of vinyl polymerizations by radical mechanisms. London: Butterworth, 1958.
[19] Macromolecules. In: Bovey FA, Winslow FH, editors. An introduction to polymer science. New York: Academic Press, 1979.
[20] Odian G. Principles of polymerisation, 2nd ed. New York: Wiley, 1981. p. 254.
[21] Matheson MS, Auer EE, Bevilacqua EB, Hart. J Am Chem Soc 1951;73:1700–6.
[22] Fukuda T, Ma Y, Inagaki H. Macromolecules 1985;18:17–26.
[23] Davis TP, O'Driscoll KF, Piton MC, Winnik MA. Macromolecules 1989;22:2785–8.
[24] Beuermann S, Buback M, Davis TP, Gilbert RG, Hutchinson RA, Olaj OF, Russell GT, Schweer J, van Herk AM. Makromol Chem Phys 1997;198:1545–60.
[25] Buback M, Kowollik C. Macromolecules 1999;32:1445–52.
[26] Olaj OF, Bitai I, Gleixner G. Makromol Chem 1985;186:2569–80.
[27] Olaj OF, Bitai I, Hinkelmann F. Makromol Chem 1987;188:1689–702.
[28] Olaj OF, Bitai I. Angew Makromol Chem 1987;155:177–90.
[29] Buback M, Kowollik C, Kamachi M, Kajiwara A. Macromolecules 1998;31:7208–12.
[30] Yamada B, Westmoreland DG, Kobatake S, Konosu O. Prog Polym Sci 1999;24:565–630.
[31] Tonge MP, Pace RJ, Gilbert RG. Macromol Chem Phys 1994;195:3159–72.
[32] O'Neil GA, Torkelson JM. Macromolecules 1999;32(2):411–22.
[33] O'Neil GA, Torkelson JM. Trends Polym Sci 1997;5:349–55.
[34] Buback M, Kurtz CH. Makromol Chem Phys 1998;199:2301–10.