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Free Radical Reactions in Poly(methyl methacrylate) Films Monitored Using a Prefluorescent Quinoline−TEMPO Sensor

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ABSTRACT: The photochemical and photophysical properties of 4-(3-hydroxy-2-methyl-4-quinolinoyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl free radical (QT) have been studied as a prefluorescent probe to monitor free radical processes in polymer films. This methodology takes advantage of the efficient intramolecular quenching of the fluorescence of quinoline by the paramagnetic nitroxide, which is disabled when TEMPO reacts with carbon-centered radicals. The fluorescence intensity−time profile observed in the thermal decomposition of 2,2′-azobis(isobutyronitrile) (AIBN) in poly(methyl methacrylate) (PMMA) films showed initial increments in the fluorescence with time, according to the trapping of carbon-centered radicals by QT in the polymer films. Comparison of data under nitrogen and oxygen saturation conditions suggests that oxygen trapping of the carbon-centered radicals at 90 °C is about 20 times faster than reaction with nitroxides. The activation energy for AIBN decomposition in PMMA was measured as 34.1 kcal/mol. Analysis of the fluorescence lifetime distribution establishes the involvement of both static and dynamic fluorescence quenching of the diamagnetic reaction product by AIBN.

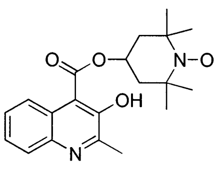
Introduction

The ability of paramagnetic nitroxides to trap efficiently carbon-centered radicals has been known for a long time,[1−3] and nitroxides have been used as scavengers to inhibit free radical polymerization and polymer degradation.[4−6] Further, reaction between the nitroxides and carbon-centered radicals[7,8] leads to *N*-alkoxyamines. Carbon−oxygen bond formation is reversible at high temperatures and has been employed to promote free radical polymerization in a controlled manner, in a process known as “living” free radical polymerization.[9−11]

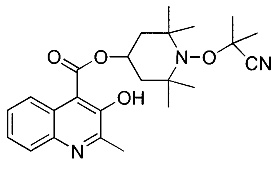
Recently, the properties of nitroxides as quencher of singlet and triplet states have been employed to design molecular switches or probes to directly monitor free radical processes.[12−15] When the paramagnetic nitroxide is covalently attached to a fluorophore moiety, the proximity of the nitroxide results in efficient intramolecular quenching of the excited state of the fluorophore. Radical trapping by the nitroxide leads to a diamagnetic alkoxyamine, thereby eliminating the intramolecular quenching and restoring the fluorescence of the chromophore, allowing a direct quantification of the free radical formation.[16−18]

In a previous report, we have illustrated the use of prefluorescent paramagnetic sensors to monitor the kinetics for end-cap cleavage in TEMPO-capped polystyrene obtained by “living” free radical polymerization.[19] In particular, this methodology has permitted monitoring of free radical polymerization in real time via fluorescence measurements and evaluation of activation parameters and bond dissociation energies directly; this approach proved simpler than those used previously.[20,21]

In the present report, we examine the properties of 4-(3-hydroxy-2-methyl-4-quinolinoyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl free radical (QT) to monitor free radical processes in polymeric films at moderately high temperatures. In particular, we propose that this methodology can be useful in studies of polymer degradation[22,23] or degradation of organic additives incorporated into polymeric matrices.[6] In fact, many chemical sensors used in polymer films to evaluate properties such as pH or temperature are based on the use of incorporated dyes; understanding the thermal and photochemical stability of the dye is crucial.[24]



QT



QT-IBN

Experimental Section

Synthesis of 4-(3-Hydroxy-2-methyl-4-quinolinoyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl Free Radical (QT). The QT sensor was synthesized by a procedure similar to that described by Hassner.[25] 3-Hydroxy-4-methyl-2-quinoline carboxylic acid was esterified with 4-hydroxy-TEMPO in the presence of 4-(dimethylamino)pyperine and 1-[(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride in CH_2Cl_2 under argon at 60 °C for 6 h. The reaction mixture was washed four times with water, then dried over magnesium sulfate, and finally concentrated. The residue was chromatographed on silica gel (hexane/ethyl acetate, gradient from 8:2 to 7:3) to obtain QT. Red crystals were obtained from saturated acetonitrile solutions of QT at −20 °C. Crystal data: $C_{20}H_{25}N_2O_4$, MW = 357.42, monoclinic, space group $P2(1)/n$, $a = 8.3137$ (6) Å, $b = 25.0697$ (2) Å, $c = 9.5088$ (7) Å, $\beta = 111.15$ (1)°, $V = 1848.3$ (2) Å^3, $Z = 4$, $\rho_{calcd} = 1.284$ mg/m^3, λ(M*o* Kα) = 0.710 73 Å, $\mu = 0.090$ mm^{-1}, $T = 173$ (2) K, $R = 0.0507$, $wR^2 = 0.0965$;[26] mp 141−145 °C. MS *m/z:* 357 (M^+, 49), 342 (3), 203 (22), 186 (97), 69 (100). Anal. Calcd for $C_{20}H_{25}N_2O_4$: C, 67.21; H, 7.05; N, 7.84%. Found: C, 67.32; H, 6.85; N, 7.65%.

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Synthesis of 3-Hydroxy-2-methylquinoline-4-carboxylic Acid 1-(1-Cyano-1-methylethoxy)-2,2,6,6-tetramethylpiperidin-4-yl (QT-IBN). The diamagnetic alkoxyamine QT-IBN was synthesized by coupling of QT with 2-cyano-2-propyl radicals derived from thermal decomposition of 2,2′-azobis(isobutyronitrile) (AIBN) in acetonitrile under a nitrogen atmosphere at 70 °C for 10 h. After evaporation of the solvent the yellow precipitate was washed three times with methanol, filtered, and recrystallized from acetonitrile at −20 °C; mp 98−100 °C. MS *m/z:* 357 (16), 342 (1), 267 (1), 203 (6), 186 (26), 158 (8), 69 (100). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 12.04 (s, 1H), 8.55 (m, 1H), 7,98 (m, 1H), 7.52 (m, 2H), 5.49 (m, 1H), 2.70 (s, 3H), 2.17 (m, 2H), 1.92 (m, 2H), 1.70 (s,12H), 1.32 (d, 6H). ^{13}C NMR (500 MHz, $CDCl_3$) δ: 171.43, 155.78, 154.00, 142.34, 129.81, 128.05, 126.43, 124.70, 124.18, 122.48, 109.08, 75.39, 69.82, 60.85, 44.87, 34.36, 27.69, 21.57, 20.61.

Polymeric Film Preparation. The polymeric films were prepared employing an extensor technique using solutions of poly(methyl methacrylate) (PMMA) of 120 000 molecular weight at 20 wt % in dichloromethane containing AIBN at 5 wt % and the prefluorescent probe (QT) at 1 wt %. A small quantity of this solution was dropped on a clean microscope slide (Fisher Scientific Co.), and the solution was extended along the slide with a calibrated rod. After solvent evaporation at room temperature, polymeric films of 20 ± 1 μm of thickness were obtained.

Temperature Dependence Studies. The thermal studies were carried out using freshly prepared polymeric films under a nitrogen or oxygen atmosphere. To achieve gas diffusion equilibration in the polymer films, the samples were maintained under nitrogen and oxygen atmospheres for 30 min before heating them on a thermostated aluminum plate (a prototype of a Luzchem LZC-BK disk heater). The reaction was stopped by cooling the polymer sample on a second aluminum plate maintained at room temperature. The fluorescence spectra of the samples were measured at room temperature using front face excitation in a Perkin-Elmer LS-50 spectrofluorimeter, employing an excitation wavelength of 350 nm in order to achieve selective excitation of the dye. The rate constants observed (k_{obs}) were obtained by monitoring the growth of the fluorescence (at 400 nm) according to the equation

$$\ln\left(\frac{I^{\infty} - I^{0}}{I^{\infty} - I^{t}}\right) = k_{obs}t \qquad (1)$$

where I^{∞}, I^0, and I^t represent the fluorescence intensities in the *plateau* region, initially, and at time "*t*", respectively.

Fluorescent Lifetimes. The time-resolved fluorescence measurements were carried out using a Hamamatsu C-4334 streakscope, allowing simultaneous spectral and time-resolved data acquisition. The excitation source was the third harmonic of a Continuum PY-61 picosecond Nd:YAG laser (355 nm, 35 ps, 3 mJ/pulse)[27] in a front-face arrangement. Lifetime distribution analysis was performed on fluorescence decays traces until only 1% of the light intensity integrated over all the fluorescent wavelength range remained. This was done using an exponential series method software package from Photon Technology International. The fitting function employed contains 100 exponential terms, which were fixed at logarithmically spaced lifetimes, from 0.04 to 30 ns with variable preexponential factors.[28]

Materials. All the chemicals were purchased by Sigma-Aldrich Canada (Oakville, ON, Canada) and used as received except were noted. The solvents were HPLC grade from Omnisolv (Gibsstown, NJ).

Results and Discussion

In the past few years, the design of molecular probes based on fluorescent nitroxide adducts has generated considerable interest in different biological and chemical fields. Recently, these probes have been used in polymer systems to monitor free radical reaction rates or evaluate kinetic parameters in "living" free radical polymerization.[19] To extend the use of these probes to free radical processes to other polymer systems, we initiated studies employing the fluorescence response of 4-(3-hydroxy-2-methyl-4-quinolinoyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl free radical (QT) to free radical processes in films. While our study centers on free radical detection, the chromophore unit in this molecule has also a high sensitivity to pH, allowing the parallel monitoring of both free radical processes and changes in pH.[29] The present studies were performed in poly(methyl methacrylate) (PMMA) films, employing 2-cyano-2-propyl radicals derived from the thermal decomposition of 2,2′-azobis(isobutyronitrile) (AIBN). The final concentrations of QT and AIBN employed in the polymeric films were rather high, but high concentrations of additives are not uncommon in polymeric films for commercial applications, particularly in thin films employed in microlithography.

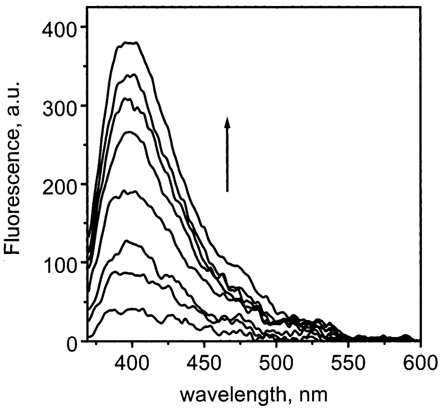


Figure 1. Fluorescence emission spectra of PMMA films doped with QT and AIBN, measured at different times of heating at 100 °C under nitrogen (λ_{exc} 350 nm). The spectra were recorded at 0, 10, 20, 30, 50, 70, 120, and 180 min.

To establish the sensitivity of QT toward carbon-centered radicals in polymer films, the reactions were carried out under nitrogen and oxygen atmospheres at different temperatures, and the fluorescence emission spectra were recorded at room temperature following each heating period in order to avoid thermal effects on the fluorescence intensity (Figure 1). The intensity of fluorescence showed monotonic increments with heating time, as expected for the reaction of the paramagnetic nitroxide with carbon-centered radicals, derived from the thermal decomposition of AIBN. In fact, the fluorescence spectra observed in the polymer films retains the same characteristics observed for reactions carried out in acetonitrile or in ethanol at room temperature, associated with the same diamagnetic product (data not shown). Further, the reaction of QT with radicals derived from the thermal decomposition of AIBN in acetonitrile under anaerobic conditions shows a quantitative formation of the product of coupling 3-hydroxy-2-methylquinoline-4-carboxylic acid 1-(1-cyano-1-methylethoxy)-2,2,6,6-tetramethylpiperidin-4-yl (QT-IBN).

The reaction was studied in a polymer matrix where the cage effect due to the high viscosity of the media plays an important role. Equations 1−6 show the expected reaction mechanism:

$$R{-}N{=}N{-}R \rightarrow [2R^{\bullet} + N_2] \qquad (1)$$

$$[R^{\bullet} + R^{\bullet}] \rightarrow R{-}R \qquad (2)$$

$$[R^\bullet + R^\bullet] \rightarrow 2R^\bullet \quad (3)$$

$$QT + R^\bullet \rightarrow QTR \quad (4)$$

$$R^\bullet + R^\bullet \rightarrow R{-}R \quad (5)$$

$$R^\bullet + O_2 \rightarrow ROO^\bullet \quad (6)$$

where eqs 2 and 3 represent the competition of radicals initially produced in the AIBN thermal decomposition that either recombine or escape the solvent cage. In particular, reaction 4 does not take into account the equilibrium at higher temperatures considered under irreversible conditions due to the high concentration of QT and cage effect. Furthermore, this is expected to have a minimal contribution for the 2-cyano-2-propyl radicals in the temperature range examined due to its lower stability (and anticipated higher bond dissociation energy) compared with that of benzyl radicals produced in the thermal decomposition of commonly employed alkoxyamines as initiators in “living” free radical polymerizations.[7,11]

Under anaerobic conditions (eqs 1−5), the increase in fluorescence with time should be directly related to diamagnetic product formation (QTR or QT-IBN)

$$dF/dt = a2k_1k_3[\mathrm{AIBN}]/(k_2 + k_3) \quad (7)$$

where a is a proportionality constant that includes the fact that the fluorescence is measured in a front-face arrangement as well as other instrumental parameters, k_1 represents the rate constant for thermal decomposition of AIBN, and $k_3/(k_2 + k_3)$ corresponds to the escape fraction of free radicals. According to this equation, at short times the fluorescence intensity responds linearly with time, reflecting the constant rate of free radical production due to the excess of AIBN employed under our experimental conditions. The emission intensity reaches a *plateau* at longer times when QT has reacted quantitatively. The observed time profiles of the fluorescence follow this behavior, showing faster increases in the rate constant observed (k_{obs}) as the temperature is increased; further, shorter times are needed to reach the *plateau* at the higher temperatures, reflecting an increase in the rate for decomposition of AIBN. However, the intensity value in the *plateau* region is temperature-dependent, with higher values as the temperature reaction increases (Figure 2), suggesting incomplete trapping of the radicals by QT due to the high viscosity of the media and/or the involvement of intermolecular fluorescence quenching mechanisms (vide infra).

The experiments carried out under oxygen show initial fluorescence growth rates lower in comparison with nitrogen at the same temperature. This suggests an incomplete trapping of the initial carbon-centered radicals by the prefluorescent probe, presumably due to a competition of the free radicals by oxygen to produce peroxyl radicals, which are nonreactive toward the nitroxide moiety.[30] In fact, the diffusion of oxygen in polymer matrices is faster than the diffusion of organic molecules,[31] and thus oxygen will compete for carbon-centered radicals, even if its concentration is lower than that of the much larger QT. Assuming that the secondary reactions of the peroxyl radicals do not affect diamagnetic product formation (eqs 1−6), it is possible to derive a kinetic expression that reflects the rate of formation of the fluorescence species, QTR.

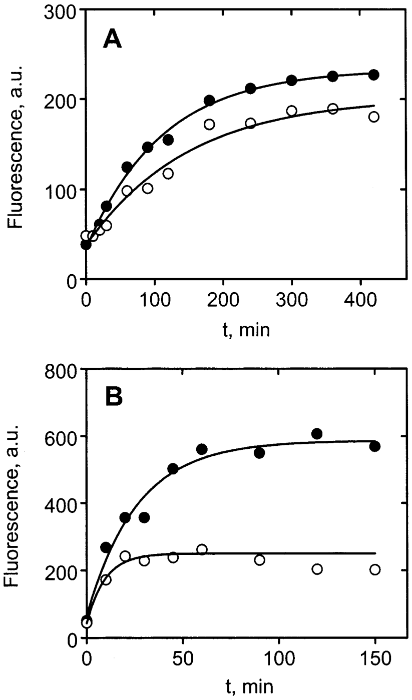


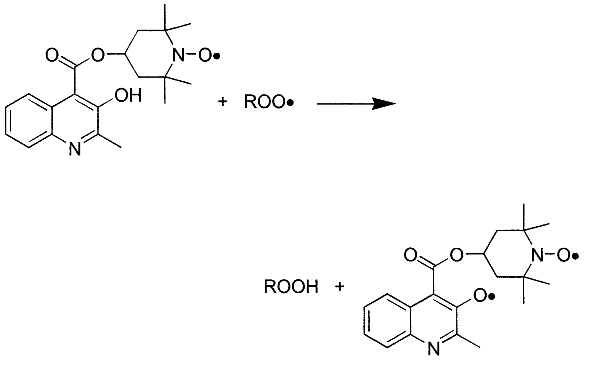
Figure 2. Time course of the fluorescence intensity measured at 400 nm (λ_{exc} 350 nm) in polymer films after reaction under a nitrogen (●) and oxygen (○) atmosphere, at 90 °C (A) and 110 °C (B). Data fitted according to eq 1.

$$d[\mathrm{QTR}]/dt = k_4 2k_3[\mathrm{QT}][\mathrm{AIBN}]k_1/((k_2 + k_3)(k_4[\mathrm{QT}] + k_6[\mathrm{O}_2])) \quad (8)$$

The lower *plateau* values in the experiments carried out under oxygen in comparison with nitrogen, at the same temperature, are related with the fraction of carbon-centered radicals reacting with oxygen. However, the increase of the *plateau* intensity with the temperature in the experiments under oxygen is lower than that observed in experiments under nitrogen; even at high temperatures the intensity at the *plateau* region under oxygen is not constant and decreases at long reaction times.

The behavior observed under oxygen at high temperatures can be partially attributed to degradation of the fluorescent group. In fact, the peroxyl radicals, while unreactive toward the TEMPO moiety, may attack the phenolic group in QT, thus destroying the fluorescent chromophore (eq 9). A similar reaction can also be written for the product QT-IBN with similar consequences. This reaction is more prominent at higher temperatures, most likely because the reaction with peroxyl radicals is faster due to both an intrinsic increase in rate constant and some decrease in the fraction of intramolecular hydrogen-bonded quinoline. However, at low temperatures and short reaction times, the influence of this secondary reaction on the fluorescence intensity is not significant in comparison to much faster scavenging of carbon-centered radicals by the nitroxide moiety. In fact, in acetonitrile, at 25 °C, the rate constant of hydrogen abstraction from phenolic groups by peroxyl radicals is ~2500 times slower than the benzyl radical trapping by TEMPO.[1,3,32,33]

Thus, it is possible derive a kinetic expression according to the mechanism previously proposed (eqs 7



(9)

and 8) to evaluate the relative radical trapping rates by QT and by oxygen at moderate temperatures, from the initial slopes of the increase of fluorescence observed under oxygen and nitrogen. In the early stages of the reaction the influence of peroxyl radicals on the fluorescence mechanism should be minor. Thus, assuming a simple kinetic competition between oxygen and QT for the carbon-centered radicals, one can derive eq 10.

$$\frac{(\mathrm{d}F/\mathrm{d}t)_{\mathrm{N_2}}}{(\mathrm{d}F/\mathrm{d}t)_{\mathrm{O_2}}} = 1 + \frac{k_6[\mathrm{O_2}]}{k_4[\mathrm{QT}]} \qquad (10)$$

From the reactions carried out at 90 °C (Figure 2A), the experimental ratio between the initial slopes under nitrogen and oxygen is 1.9, and considering the initial concentration of QT 0.1 M and the oxygen concentration of 0.01 M, estimated from homogeneous solvents for the polymer film at 1 atm of oxygen pressure at 25 °C,[34-36] a rough value for $k_6/k_4 \sim 10$ is obtained. Although the oxygen concentration was not measured in the present work, this value allows us to establish a lower limit for the rate constants ratio due the influence of the temperature over the oxygen solubility in the polymer film. In fact, from the oxygen solubility coefficient dependence with the temperature in similar polymeric films, it is possible to estimate a decrease in the oxygen solubility by a factor of 2 when the temperature is increased from 25 to 90 °C,[37] giving a value of $k_6/k_4 \sim 20$ at 90 °C. This value is considerably lower compared with data found in organic polar solvents for TEMPO, as acetonitrile ($k_6/k_4 \sim 35$) for benzyl radicals or alkyl radicals ($k_6/k_4 \sim 32$).[1,32,38] It is important to note that the rate constant observed for carbon-centered radicals trapping by TEMPO evaluated in nonpolar solvent, such as hexane, is faster than in polar solvents ($k_6/k_4 \sim 10$). However, because of the polarity of poly(methyl methacrylate), the rate constant ratios are comparable with those for polar solvents, such as acetonitrile or ethyl acetate. Thus, the values in the rate constant ratio estimated in the polymer films suggest an influence of the slower diffusion of the radicals in the polymer matrix, decreasing the rate of carbon-centered radicals trapping by QT, in comparison with homogeneous solvents. This is not surprising, since the effect should be larger for the larger molecules in comparison with the highly mobile oxygen molecule.

To evaluate whether the dependence of the *plateau* intensity value with the temperature was due to incomplete radical trapping by the probe at lower temperatures, we determined the fluorescence lifetimes. The fluorescence decays were measured in polymer films doped with QT and AIBN under the conditions where the florescence reached the *plateau* region in low-temperature reactions. This should maximize any effects on the reaction between carbon-centered radicals and QT due to restricted diffusion.

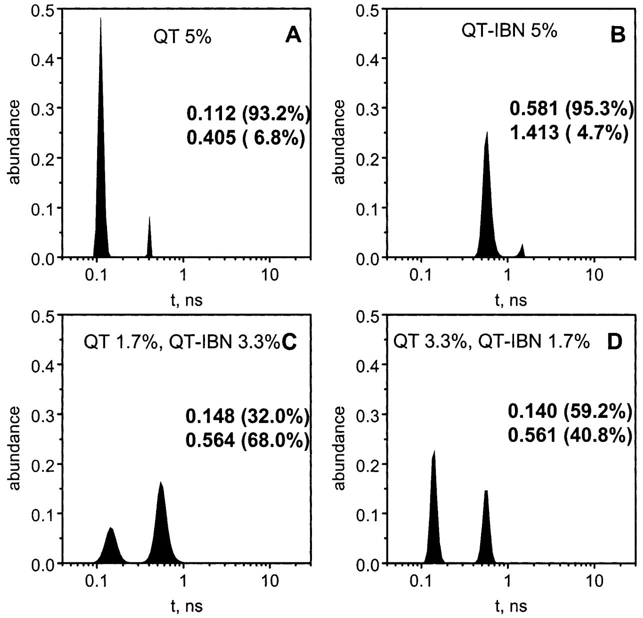


Figure 3. Lifetime distribution in polymer films: (A) QT 5 wt %; (B) QT-IBN 5%; (C) QT 1.7%, QT-IBN 3.3%; (D) QT 3.3%, QT-IBN 1.7% (% by weight). The lifetime distributions were evaluated from fluorescence decays observed employing 355 nm laser excitation (see Experimental Section).

The fluorescence decays of QT and QT-IBN in films did not fit to monoexponential decays, showing the presence of more than one microenvironment for the probes. The fluorescence decays measured in the polymer films were analyzed in terms of distribution of the fluorescence lifetimes to evaluate the different environments for the probes (see Experimental Section). The distribution of the fluorescence lifetime analysis of QT and QT-IBN in the polymeric films showed narrow distributions of the fluorescence lifetime centered at 110 and 580 ps, respectively (Figure 3A,B), which are slightly different than the fluorescence lifetimes of QT and QT-IBN measured in dichloromethane (70 and 600 ps, respectively). In particular, all the measurements of QT presented a small contribution to the fluorescence of one component of longer lifetimes, suggesting small levels of diamagnetic impurities in QT. In fact, the longer component observed in QT samples shows similar fluorescence spectra to QT-IBN. The difference in the lifetime for the diamagnetic impurity relative to the value measured for the diamagnetic compound is within the error limits for the lifetime distribution method employed. However, the shorter lifetime of the diamagnetic impurity could reflect an intermolecular quenching by the paramagnetic nitroxide QT. To evaluate whether intermolecular quenching by QT could play some role, fluorescence lifetimes were measured with different proportions of QT and QT-IBN in the polymeric films and analyzed. They did not show changes in the fluorescence lifetime of the QT-IBN, thus ruling out possible intermolecular quenching by QT under our experimental conditions (Figure 3C,D). Nonetheless, at much higher concentrations of the nitroxide, a decrease of the average lifetime of the diamagnetic compound was observed due to intermolecular fluorescence quenching by QT (data not shown).

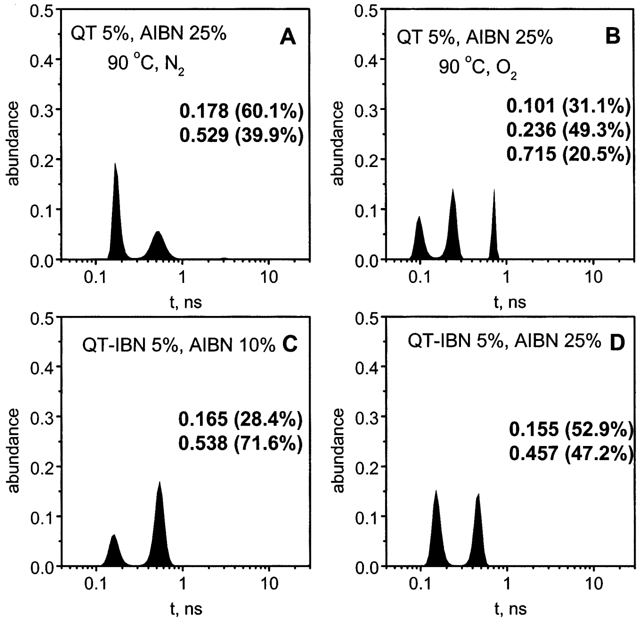


Figure 4. Lifetime distribution in polymer films: (A) QT 5% and AIBN 25 wt %, after reaction under nitrogen at 90 °C per 400 min; (B) QT 5% and AIBN 25%, after reaction under oxygen at 90 °C per 400 min; (C) QT-IBN 5%, AIBN 10%; (D) QT-IBN 5%, AIBN 25% (% by weight). The lifetime distributions were evaluated from fluorescence decays observed employing 355 nm laser excitation (see Experimental Section).

After reaction under nitrogen, the fluorescence lifetime distribution in the films doped with QT and AIBN showed complete reaction of QT with the carbon-centered radicals derived from AIBN, as can be observed by the absence of short lifetimes corresponding to the paramagnetic compound (Figures 3 and 4). This result suggests that the temperature dependence of the intensity of the plateau observed in the fluorescence time profile is not due to an incomplete reaction of QT in the reactions under nitrogen. On the other hand, the presence of an ensemble with shorter lifetime (110 ps) in reactions carried out in the presence of oxygen shows incomplete reactions of QT, due to carbon-centered radical reaction with oxygen, to produce peroxyl radicals, which are in turn unreactive toward nitroxides. Interestingly, the reactions carried out under nitrogen as well as under oxygen presented the contribution of a lifetime population shorter than the lifetime corresponding to the diamagnetic reaction product in polymer films, ca. 200 ps (Figure 4A,B). Experiments carried out at several concentrations of the diamagnetic compound QT-IBN from 5 to 10 wt % showed only one population with an average lifetime at 600 ps, ruling out an interaction between the fluorescent diamagnetic molecules that could be reflected in the fluorescence lifetime distributions (data not shown).

Films prepared with QT-IBN and different concentrations of AIBN exhibited decreasing fluorescence intensity with the increasing AIBN concentration; this can be attributed to quenching of the fluorescence from QT-IBN by AIBN. The distribution of fluorescence lifetimes showed increased importance of the shorter lifetime contribution (ca. 200 ps), and shorter lifetimes of the longer component associated with QT-IBN (from 580 to 460 ps), with increasing AIBN concentration (Figure 4C,D).

Thus, the ensemble with shorter lifetime (ca. 200 ps) observed in the reactions carried out under nitrogen and oxygen can be associated with static quenching mechanisms caused by AIBN in close proximity to QT-IBN. Considering that the quencher molecules closest to the fluorophore quench instantaneously the fluorescence of the fluorophore after excitation and that those molecules are distributed in a Poisson distribution in a volume V' around the fluorophore, the following expression of combined static and dynamic quenching is obtained:

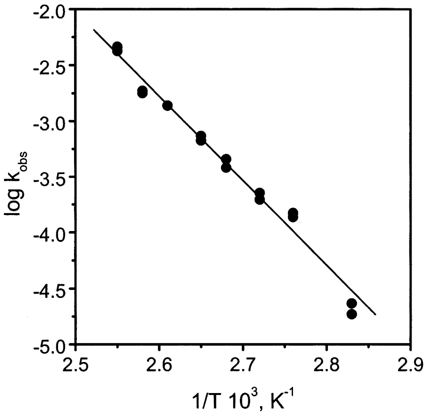


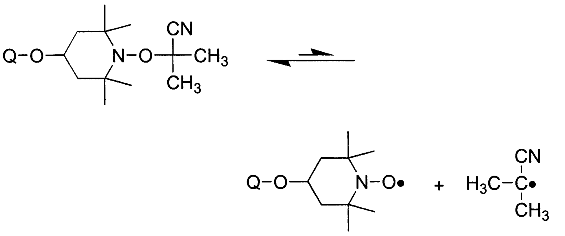
Figure 5. Arrhenius plot for the determination of the activation parameters for the thermal decomposition of AIBN in PMMA films evaluated from fluorescence measurements in the presence of QT under a nitrogen atmosphere.

$$I_o/I = (1 + K_{SV}[Q])\exp([Q]V)$$

where K_{SV} is the Stern–Volmer quenching constant, expressed as the product of the bimolecular quenching rate constant (k_q) per fluorophore decay lifetime in the absence of the quencher (τ_0), and V is the static quenching constant ($V = V'N_A$, where V' corresponds to the volume around the fluorophore and N_A is Avogadro's number). However, in the thermal reaction the quencher (AIBN) is consumed as the reaction progresses, and both mechanisms of quenching (static and dynamic) diminish with time. According to this quenching mechanism, the plateau region reflects the quantitative reaction of QT, at least in the experiments under nitrogen; however, the intensity value in the plateau region should not be constant, increasing with the time as the AIBN still present undergoes thermal decomposition.

While the fluorescence profile can be complex due to the quenching processes in our system, the initial rate of the fluorescence growth should be quenched to the same extent independent of the temperature (remember the actual measurements are always at room temperature); thus, the experimental rate constants, k_{obs}, estimated at lower conversions, should be proportional to the rate constant of QT-IBN formation. An Arrhenius plot of the experimental rate constants derived from the experiments under nitrogen allows the estimation of an activation energy of 34.1 kcal/mol for AIBN decomposition in the polymer films (Figure 5). The difference between the activation energy determined in polymer films and the value of 31.3 kcal/mol reported in toluene[39] is probably due to the constraints imposed by the polymer media. In fact, this value is influenced by the dependence of the radical escape from the cage ($k_3/(k_2 + k_3)$) due to change in the viscosity of the polymer media with the temperature. However, the high concentration of additives present in the polymer films reduces the T_g of the polymer below the interval of temperatures employed in the present study,[31] as is suggested by the linearity in the Arrhenius plot, and the fraction of escape of the radical from the cage should be relatively constant in the temperature range evaluated. Even if the cage effect change would double, in the range of temperature evaluated, the activation energy would only change by less than $^{1}/_{2}$ kcal/mol.

Interestingly, the activation energy for AIBN decomposition is close to the activation energy of C−O bond dissociation in *N*-alkoxyamines. In fact, these activation energies measured, for different *N*-alkoxyamines in homogeneous solvents and in "living" free radical polymerization, are close to 30 kcal/mol, and the activation energy estimated for radical trapping by TEMPO compounds is around 2 kcal/mol.[7,8,19] In the present kinetic model this reaction has been assumed to occur under irreversible conditions due the excess of QT employed initially and the fact that the radicals trapped do not have the benzyl radical character common in previous studies. To evaluate whether at higher temperatures in the plateau zone, where QT has consumed completely, the reversibility of this reaction could take place in the polymer film (eq 11), thermal experiments were performed employing films doped with QT-IBN. However, the fluorescence intensities and the distribution of lifetimes did not change with time, ruling out any formation of QT from QT-IBN decomposition (data not shown). In fact, the activation energies establish the equilibrium conditions, but the radicals are restricted in their escape from the solvent cage in the polymer film, recombining again, assisted by the high viscosity of the media. This effect has been previously reported in photochemical cleavages that are masked by the rapid back-reaction, in homogeneous solution, and described as a persistent radical effect.[40] In the case of AIBN the situation is somewhat different, since the nascent free radicals are separated by the simultaneous formation of nitrogen, thus increasing the fraction of radicals that escape the solvent cage.



(11)

In conclusion, the use of the prefluorescent nitroxide probe, QT, has permitted monitoring free radicals generated thermally from AIBN in PMMA films via fluorescence measurements. This methodology allows the acquisition of kinetic information such as the activation energy of AIBN decomposition in polymeric films. The fluorescence lifetime distribution analysis shows both dynamic and static fluorescence quenching by AIBN. For that reason, the presence of fluorescence quenchers in more complex systems (such as polymeric films employed in microlithography) would require complementary methodologies to quantified the quencher effect over fluorescence measurements. The use nitroxide probes with pH-sensitive chromophores could be very useful in microlithography, where photoacid generation and free radical processes can be monitored simultaneously.

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