Polymerization of acrylic and methacrylic monomers using $\text{CF}_3\text{OC(O)OO(O)COCF}_3$ as radical initiator

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(Received: 27 April, 2007; published: 8 June, 2007)

Abstract: The study of $\text{CF}_3\text{OC(O)OO(O)COCF}_3$ as radical initiator in polymerization of acrylic and methacrylic monomers as acrylic acid (AA), acrylonitrile (AN), 2-hydroxyethyl methacrylate, (HEMA), and methyl methacrylate (MMA), is presented. The reactions were carried out under different conditions in order to explore the efficiency of the initiator. The results demonstrated that the yield and the type of the products (soluble or non-soluble) is dependent on the reactivity and the solubility of the initiator in the monomers, constituting a heterogeneous system influenced by hydrophobic-hydrophilic balance of the species involved.

Introduction

In the last decades, the conservation of the environment, the innovation in technological processes that avoid the use of solvents as well as the chemical recycling, among many other issues, have become one of the most interesting challenges for research groups in the field of materials aiming at the study of alternative processes and economical solutions [1-4].

Since the very beginning of the chemistry of polymers a great importance has been laid on the discovery of new initiators that would allow obtaining of polymers in high yields and with interesting physical and chemical properties both quickly and affordably [5]. Very recently, the use of perfluoroalkyl compounds in radical reactions has increased due to the availability of perfluoro diacyl peroxides suitable to be used as initiators [6 and references therein]. This type of initiators could offer many advantages since they could produce cleaner and faster reactions. The thermal decomposition has been so far the preferred method due to the modest temperatures required to initiate the reaction compared to the analogous hydrogenated diacyl peroxides.

Bis(trifluoromethyl)peroxy dicarbonate, $\text{CF}_3\text{OC(O)OOC(O)OCF}_3$, is a very clean thermal source for $\text{CF}_3\text{O}\cdot$ radicals, as demonstrated by Argüello *et al* [7], and García *et al* [8]. The synthesis and characterization of this molecule was important from the point of view of the intermediate produced in reactions that involve catalytic oxidation of CO mediated by CF_3O_x ($x = 1,2$) radicals which are in turn generated by the degradation of chlorofluorocarbon and hydrofluorocarbon molecules.

The only known use of $\text{CF}_3\text{OC}(\text{O})\text{OOC}(\text{O})\text{OCF}_3$ as initiator comes from Souzy *et. al.* [9], who reported the synthesis of polyvinylidene fluoride. In that work, a very complete spectroscopic characterization of the products and mechanism of polymerization was presented where the addition of the radical $\text{CF}_3\text{O}\cdot$ to the monomer was proved.

In this paper we present the results obtained from the studies of polymerization of methacrylic and acrylic type monomers using $\text{CF}_3\text{OC}(\text{O})\text{OOC}(\text{O})\text{OCF}_3$ as the radical initiator. The products obtained were chemically characterized and quantified. The reactivity and the ability of the initiator were analyzed through a comparison in type and the quantity of the products observed.

Results and discussion

The compound studied as radical initiator in this work Bis(trifluoromethyl)peroxy dicarbonate, $\text{CF}_3\text{OC}(\text{O})\text{OOC}(\text{O})\text{OCF}_3$, is a recently isolated substance that was synthesized and characterized pursuing information about atmospheric chemistry [7]. Its thermal decomposition gives rise to the formation of $\text{CF}_3\text{OCO}_2\cdot$ radicals which decarboxylate very rapidly to give $\text{CF}_3\text{O}\cdot$ radicals. These radicals are the actual initiators of the polymerization reaction and their formation is depicted in Scheme 1. The temperatures needed to cleave the acyl peroxide are relatively low (at 60 °C the half life of the gaseous molecule is 190 min and at 70 °C it drops to 55 min [8]) and any temperature higher than room temperature assures the complete decarboxylation to yield the $\text{CF}_3\text{O}\cdot$ radical.

Scheme 1. Formation of $\text{CF}_3\text{O}\cdot$ radical [8].

The different polymeric products were obtained by heterophase (liquid/gas) bulk reaction polymerizations. The monomers used (HEMA, AA, AN and MMA), as well as some relevant experimental conditions are gathered in Table 1. In all cases, $\text{CF}_3\text{OC}(\text{O})\text{OOC}(\text{O})\text{OCF}_3$ was used as initiator at 60 °C. The products obtained under the conditions shown in Table 1 were polyHEMA, polyAA, polyAN, and polyMMA. As it is shown, both yield and nature of product (soluble or non-soluble) are very different for each kind of monomer.

When HEMA was used as monomer, a particular feature was observed. A high reactivity of the initiator with the formation of relatively short polyHEMA chains (mean molecular weight, $M_w=23\,800$) is seen together with the cross-linking product at times of around 10 min.; while at longer times (30 min), all the short chains are cross-linked leaving no soluble residue. Taking these observations into account, further reactions were performed with the other monomers at approximately the same conditions where 100 % yield of polyHEMA was observed (0.5 mol % of initiator, 60 °C and 30 min.). All of them presented a much lower reactivity than HEMA. In the case of AA, the yield observed (19%) is the highest for all the three other monomers at 30 min. Nevertheless, comparing experiments at the same time (120 min) but at higher concentration of initiator, similar yields were obtained (46 % as compared to (20 + 30) %) with the formation of the cross-linked product at the expense of the soluble one.

Tab. 1. Reactivity of the initiator $\text{CF}_3\text{OC}(\text{O})\text{OOC}(\text{O})\text{OCF}_3$ at 60 °C.

Monomer	Initiator mol (%)	Reaction Time (min)	Polymerization yield (%)	Type of product
HEMA	0.5	10	52 ^a	Soluble in THF
			28	<i>Cross-linked</i>
	0.5	30	100	<i>Cross-linked</i>
AA	0.7	30	19	Soluble in DMF
	0.3	120	46 ^b	Soluble in DMF
	0.5	120	20	Soluble in DMF
			30	<i>Cross-linked</i>
AN	0.5	30	6	Soluble in DMF
	0.5	120	57	Soluble in DMF
MMA	0.5	30	< 1	Soluble in Benzene
	0.5	840	14	Soluble in Benzene
	5	30	17	Soluble in Benzene

^a $M_w = 23800$, $M_n = 5870$, ($M_w/M_n = 4$, characteristic of radical polymerization process); ^b $M_w > 1$ million.

For AN, the yield increases with time, and practically no cross-linking product is formed. In this particular case, the product is only formed in the surface of the container, due to the high vapor pressure of the AN at 60 °C (b.p. 77 °C). Finally, when MMA with a 0.5 mol % initiator concentration was used even at times as long as 840 min, the reaction yields were very low and only with considerable increase in the concentration of the initiator (5 mol %), better yields could be obtained.

Tab. 2. Polymerization of HEMA. Dependence of the gel yield with different reaction parameters.

Initiator mol (%)	Temp. (°C)	Reaction Time (min)	Gel yield (%)
0.5	60	10	28 ^a
0.5	60	30	100 ^a
0.5	40	360	10
0.5	25	1140	< 1
0.25	60	10	10

^a from Table 1

Taking into account the reactivity of the initiator vs HEMA in contrast to the rest of monomers studied, further experiments (just for HEMA) were carried out spanning different experimental conditions. These results are shown in Table 2. Especially, gel yields (insoluble products) were compared in order to search for a possible dependence on the amount of initiator and temperature with cross-linked products. As can be seen, even at temperatures as low as 40 °C (minimum temperature required to observe polymerization) there is cross-linked polymer production, though

at longer times. Table 2 also shows that the gel yield increases either with temperature and reaction time for a fixed concentration of initiator or when this concentration is increased.

The relatively fast appearance of cross-linked products in the polymerization of HEMA and AA initiated by $\text{CF}_3\text{OC(O)OOC(O)OCF}_3$ could be indicative of a competitive reaction path. As an example, the proposed reactions involving HEMA are shown in Scheme 2. On one hand, reaction (4) represents the most probable way for cross-linking. On the other hand, it is known that cross-linking reactions could also be produced by HEMA dimers, though we discard this possibility given the exhaustive purification of monomer previous to polymerization. Besides, the presence of the dimer leads to slight cross-linked product, if distilled HEMA is used, as was informed by other authors [10 and references therein]. In addition, we have specifically searched for the competitive path carrying out an experimental run using pure and dry linear polyHEMA (separated from the mixture of a previous experiment) in the presence of the initiator and acetonitrile as solvent. The reaction was carried out at 60 °C for two hours and the result was 75% of insoluble product.

Scheme 2. Propagation and grafting pathway.

Conclusions

In this work, we studied the ability of $\text{CF}_3\text{OC(O)OOC(O)OCF}_3$ as radical initiator in the polymerization of vinyl monomers such as HEMA, AA, AN and MMA. A close look at the system studied shows that we are in the presence of heterophase polymerization; the hydrophilic-hydrophobic conditions are a complicated mix influenced by properties of the monomer(s) and polymer(s), the initiating species, temperature, etc [11, 12]. In this sense, $\text{CF}_3\text{OC(O)OOC(O)OCF}_3$ is a highly hydrophilic molecule, therefore, its affinity or solubility in hydrophilic monomers is higher than in hydrophobic ones. The trend in product yields observed (HEMA > AA > AN > MMA) is similar to the trend in hydrophilicity of the monomers studied. In the more hydrophilic monomers such as HEMA and AA, a higher solubility of initiator together with its high dissociation constant gives rise to a significant concentration of

free radicals in the liquid phase. As a consequence, initiator is not only available to attack double bonds but also to react with growing polymeric chains, giving rise to secondary transfer and cross-linking reactions. MMA is a monomer which is easily initiated and propagated in radical polymerization in organic medium [12]. Nevertheless, in our experiments, polyMMA is only found in low yields in the conditions assayed. A particular behavior was observed for AN, where good yield was found at long times by reaction between the initiator and the monomer in the gas phase, where a homogeneous polymerization occurred. These results would indicate that $\text{CF}_3\text{O}\cdot$ is an interesting initiator to obtain hydrophilic gels with good yields, at low temperature (40-60 °C) and short reaction time.

Experimental part

Equipments

Fourier Transform Infrared Spectra (FT-IR) were carried out in a Nicolet 5-SXC FT-IR spectrometer on KBr discs. Nuclear Magnetic Resonance Spectra (NMR) were obtained in a Bruker 200 MHz NMR spectrometer.

The molecular weight distribution and the mean molecular weights of the soluble products were determined by size exclusion chromatography (SEC) with a LKB-2249 instrument at 25 °C, using refractive index Waters R401 as detector (courtesy of Dr. M.S. Cortizo, INIFTA, La Plata, Buenos Aires). For polyHEMA, a series of three μ -Styragel columns, ranging in pore size 100, 500, 10^4 Å², were used with THF as eluent. The flow rate was 0.5 ml/min. The calibration was carried out with polyMMA standards. For polyAA, a series of two NOVEMA 3000-HEMA 40 columns, were used with HAc-NaAc 0.02M as eluent. The flow rate was 1 ml/min. The calibration was done with pullulan and polyAA standards with molecular weights of lower than 1 million.

Materials

Monomers methyl methacrylate (MMA), Merck; acrylonitrile (AN), Carlo Erba, p.a.; and acrylic acid (AA), BASF, were dried over CaH_2 , distilled under reduced pressure and stored at 4 °C; monomer 2-hydroxyethyl methacrylate (HEMA), Merck, was purified as described by Beers *et al* [13]. The procedure involved washing an aqueous solution (25 vol % HEMA) of monomer with hexanes (4 x 200 mL), salting the monomer out of the aqueous phase by addition of NaCl, drying over MgSO_4 , and distilling under reduced pressure.

The following chemicals were purchased and used as received: solvents tetrahydrofuran (THF), N,N-dimethylformamide (DMF), diethyl ether, and benzene, Cicarelli, p.a.; ethanol, acetone, and acetonitrile, Sintorgan, p.a, dimethylsulfoxide (Me_2SO , d_6), Merck.

The initiator, $\text{CF}_3\text{OC}(\text{O})\text{OOC}(\text{O})\text{OCF}_3$, was synthesized and purified as explained elsewhere. Herein we offer a brief explanation [8]: it was prepared using a 5 L round-bottom glass flask with a central double-walled water-jacket quartz tube inside, where a 40 W low pressure Hg lamp was placed. The reagents used were perfluoroacetic anhydride, CO and O_2 in a typical ratio of 1:10:100 and the photolysis was carried out until the IR bands of the anhydride disappeared. The purification from the side products formed during the reaction was achieved by trap to trap distillation in vacuum.

Polymerization procedure

The procedure was as follows: 1 mL of monomer, either HEMA, AA, AN or MMA was introduced into a 100 mL round flask having a high vacuum stopcock. The flask was connected to a vacuum line, frozen with liquid nitrogen and thoroughly degassed. Then, the appropriate amount of initiator, measured through the drop in pressure from a calibrated volume (105 mL), was added. Typical amounts varied from 0.25 to 5 % in mol (as for monomer). It is worth noting that $\text{CF}_3\text{OC}(\text{O})\text{OOC}(\text{O})\text{OCF}_3$ is liquid at room temperature (boiling point 73 °C [8]); nevertheless, the pressures involved for a 0.25 to 5 % concentration (1 to 20 torr) were always well below the vapor pressure, so the initiator was always in the gaseous phase. The mixture was allowed to react, under sustained stirring, either at ambient temperature, 40, or 60 °C for the time selected for that particular run. All the experiments were carried out in bulk under different reaction conditions. Hence, temperature, time, type and percentage of initiator and type of monomer were varied as shown in Tables 1 and 2.

The polyHEMA, once obtained, was washed with different THF aliquots (which were kept for further investigation) to remove the non-reacted monomer and the soluble polymer from the gel fraction. The latter, was dried and weighed to calculate the yield and then small fractions were introduced in different solvents to test the solubility. The THF aliquots used to wash the polymer were treated with diethyl ether to precipitate the low molecular weight polymer formed.

The polyAN was dissolved in DMF and precipitated from ethanol; the polyMMA dissolved in benzene and precipitated from ethanol while the polyAA dissolved in DMF and precipitated from acetone.

Every precipitated polymer sample was centrifuged and dried to constant weight to have the yield of reaction.

Characterization of the products

FT-IR (KBr): polyHEMA, soluble fraction: 3460 (s, OH), 1717 (vs, C=O), C=C band disappearance at 1637 cm^{-1} ; polyMMA: 1727 (vs, C=O), C=C band disappearance at 1639 cm^{-1} ; polyAN: 2243 (s, $\text{C}\equiv\text{N}$), C=C and $\text{C}=\text{CH}_2$ bands disappearance at 1610 and 963 cm^{-1} respectively; polyAA, soluble fraction: 3094 (s, $\text{C}=\text{OOH}$), 1723 (vs, $\text{C}=\text{OOH}$), , C=C band disappearance at 1635 cm^{-1} .

^{13}C NMR (200 MHz, $\text{Me}_2\text{SO}-d_6$): polyHEMA (soluble fraction, 0.5% mol init., 60°C, 10 min., see Table 1): δ = 16-29 (CH_3), 32 (CH), 44 (CH_2), 58 (CH_2OH), 66 ($\text{C}=\text{OOCH}_2$), and 177 ($\text{C}=\text{OO}$). ^{13}C NMR (200 MHz, CDCl_3): polyMMA (5% mol init., 60°C, 30 min., see Table 1): δ = 16-19 (CH_3), 44-45 (CH_2), 51-54 ($\text{C}=\text{OOCH}_3$), and 177-178 ($\text{C}=\text{OO}$).

Acknowledgements

We are indebted to CONICET and SECyT-UNC for financial support. The authors also thank Dr. Maria Susana Cortizo (INIFTA, Facultad de Ciencias Exactas, Universidad Nacional de La Plata) for the molecular weight assays, Dr. Cecilia I. Alvarez Igarzabal, Dr. Marisa Martinelli (Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba) and Dr. Bruno Ameduri (Laboratory of Macromolecular Chemistry, Montpellier, France) for the helpful discussions.

References

- [1] Haaf, F.; Breuer, H.; Achte, A.; Schmitt, B.J.; Stabenow, J. *Jour. Sci. Ind. Res.* **1981**, 40, 659.
- [2] Timpe, H.; Strehmel, B.; Schiller, K.; Stevens, S. *Makromol. Chem. Rapid. Commun.* **1988**, 9, 749.
- [3] Kannurpatti, A.; Lu, S.; Bunker, G.; Bowman, C. *Macromolecules* **1996**, 29, 7310.
- [4] Gerasimov, T. G.; Snavely, D. L. *Macromolecules* **2002**, 35, 5796.
- [5] Cerna, J.; Morales, G.; Eyler, G.N.; Cañizo, A.I. *J. App. Polym. Sci.* **2002**, 83, 1.
- [6] Galimberti, M.; Barchiesi, E.; Navarrini, W. *J. Fluor. Chem.* **2005**, 126, 587.
- [7] Argüello, G.A.; Willner, H.; Malanca, F.E. *Inorg. Chem.* **2000**, 39, 1195.
- [8] García, P.; Willner, H.; Burgos Paci, M.A.; Argüello, G.A.; *Int. J. Chem. Kinet.* **2003**, 35, 15.
- [9] Souzy, R.; Ameduri, B.; von Ahsen, S.; Willner, H.; Argüello, G.A. *J. Fluorine Chem.* **2003**, 123, 85.
- [10] Huang, C.W.; Sun, Y.M.; Huang, W.F. *J. Polym. Sci. A: Polym. Chem.* **1997**, 35, 1873.
- [11] Imroz Ali, A.M.; Tauer, K.; Sedlak, M. *Polymer* **2005**, 46, 1017.
- [12] Hu, S.; Brittain, W.J. *Macromolecules*, **2005**, 38, 6592.
- [13] Beers, K.L.; Boo, S.; Gaynor, S.G.; Matyjaszewski, K. *Macromolecules* **1999**, 32, 5772.