Polymerization of Methyl Methacrylate through Ionizing Radiation in CO_2-Based Dense Systems.

Giuseppe Filardo,*,[†] Giuseppe Caputo,[†] Alessandro Galia,[†] Elio Calderaro,[‡] and Giuseppe Spadaro[†]

Dipartimento di Ingegneria Chimica Processi e Materiali and Dipartimento di Ingegneria Nucleare, Viale delle Scienze, 90128 Palermo, Italy

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ABSTRACT: Herein, we report the use of ionizing radiation to induce a dispersion polymerization reaction in dense CO_2. As a model system, the polymerization of methyl methacrylate in the presence of poly(dimethylsiloxane) stabilizers was investigated. It was demonstrated that the dose plays the key role in the progress of the reaction and in the morphology of the resulting polymer. Dispersion polymerization carried out in the presence of mono- and bifunctionalized surfactants gave differently structured polymers. The polymers obtained have been characterized by scanning electron microscopy, solubility tests, and gel permeation chromatography, and the molecular structure has been related to dynamic mechanical behavior in the melt state.

Introduction

Polymerization in dense CO_2 is not a so-called “new topic” in polymer synthesis. The first examples of the utilization of carbon dioxide as medium for polymerization reactions have been reported in the patent literature[1,2] in the second half of the 1960s. Vinyl monomers such as vinyl chloride, styrene, methyl methacrylate, acrylonitrile, acrylic acid, and vinyl acetate were polymerized or copolymerized at temperatures in the range 20−50 °C by Fukui et al.[2] Continuous ionizing radiation or typical free-radical initiators were employed, and yields ranging between 15 and 100% were reported. In the experimental conditions adopted, at least in the presence of two phases, precipitation polymerization occurred as indicated by the powdered material recovered from the reactor in many cases. Apart from the advantages in the separation procedures, the essential feature of the inertness of the carbon dioxide, not only as radical scavenger but also toward the ionizing radiation, was clearly identified.[3,4] Some other contributions during the eighties added more defined data to this previous knowledge.[5−7]

A second paramount contribution in the field is due to the work by De Simone and colleagues. The seminal paper “Synthesis of fluoropolymers in supercritical carbon dioxide”[8] by this author describes the first homogeneous free-radical polymerization in supercritical CO_2 of 1,1-dihydroperfluorooctil acrylate (FOA) to polyFOA. Copolymers with styrene, methyl methacrylate (MMA), butyl acrylate, and ethylene are also reported. It is relevant that also the fluorinated copolymers are soluble in supercritical (sc) CO_2, even if homopolymers (i.e., PMMA, PS, etc.) are insoluble in liquid or supercritical CO_2 even in severe temperature and pressure conditions.[9a]

It is worth noting that the free-radical initiator azobisisobutyronitrile (AIBN), usually employed in these polymerization reactions, imposes a threshold temperature for acceptable polymerization kinetics.

Following the paper by De Simone et al., numerous works have been done both in polymerization reactions in liquid or $scCO_2$, as reported in recent exhaustive reviews.[9b,10] Particular attention has been paid to the design of properly tailored, CO_2-soluble, amphipathic surfactants. Apart from the fluorinated surfactants, less expensive siloxane-based macromonomers have also been used as an alternative in some dispersion polymerization reactions in CO_2. Polymers such as PMMA and PS have been isolated as discrete, uniform microspheres with diameters within the range 0.1−10 μm.[11]

Other heterogeneous polymerization reactions include the ring-opening metathesis polymerization of norbornene,[9b] the cationic polymerization of cyclic and vinyl ethers and styrene,[9b,10,12,13] the carbocationic polymerization of isobutylene,[14] and the solid-state polymerization of polycarbonates.[15]

Here, we present the preliminary results about an example of polymerization reaction in CO_2-based dense systems, in the presence of surfactants, initiated by ionizing radiation. The reaction model we chose is the polymerization of MMA in the presence of polysiloxane-based surfactants.

It is well-known that the ionizing radiation can be employed versatilely in the field of polymerization and polymer processing.[16−17] We want to underline here the possibility offered by ionizing radiation to realize, through the tunable quantities (e.g., dose rate and dose), “cold polymerization processes” in mild conditions of pressure and temperature, in which operating density values can be varied in a wider range. In fact, ionizing radiation takes advantage of the fact that it does not usually require the use of chemical initiators and solvents to be active and, if properly used, is environmentally and energetically safe. Moreover, it is possible to irradiate continuously during the reaction time, and at beginning or during the process.

Experimental Section

Materials. Methyl methacrylate obtained from Merck was distilled to remove the inhibitor before use. Tetrahydrofuran (HPLC grade) and cyclohexane obtained from Riedel-de-Haën and poly(dimethylsiloxane)−monomethacrylate (PDMS−mMA)

[†] Dipartimento di Ingegneria Chimica Processi e Materiali.
[‡] Dipartimento di Ingegneria Nucleare.

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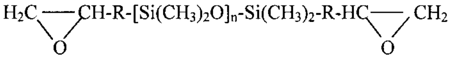
-Tegomer V-Si 2250 (M_n =2000 g/mol) and Sb1784 (M_n =20000 g/mol):

CH_2=CH-COO-R-[Si$(CH_3)_2$O]$_n$-Si$(CH_3)_2$-R-OOC-CH=CH_2

-Tegomer AMG 006 (M_n =1000 g/mol) and Sb1785 (M_n =20000 g/mol):

CH_3COO-R-[Si$(CH_3)_2$O]$_n$-Si$(CH_3)_2$-R-OOCCH_3

-Tegomer E-Si 2330 (M_n =2400 g/mol)



H_2C—CH-R-[Si$(CH_3)_2$O]$_n$-Si$(CH_3)_2$-R-HC—CH_2 (O bridging each C—C)

-PDMS (M_n =10000 g/mol)

CH_2=CCH_3-COO-C_3H_6-Si$(CH_3)_2$-[Si$(CH_3)_2$O]$_n$$C_4H_9$

Figure 1. Chemical formulas of polysiloxane stabilizers.

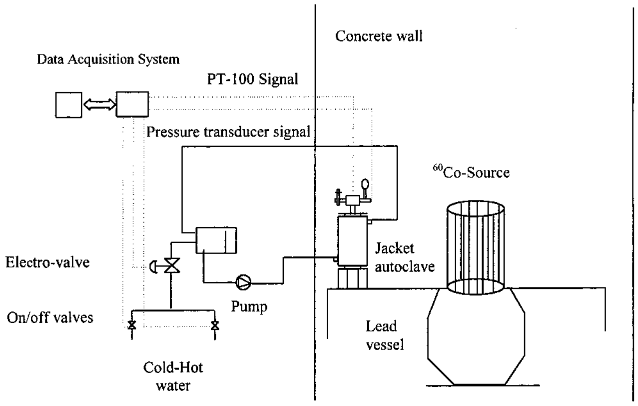


Figure 2. Scheme of the IGS-3 γ-irradiator facility.

with M_n ~ 10000 g/mol obtained from Aldrich were used as received. Tegomer V-Si2250, E-Si2350, AMG006, Sb1784,and Sb1785 were obtained from Th. Goldschimdt A.G. (see Figure 1). Carbon dioxide was SOL 99.997%. Conventional PMMA was obtained from Rhom and Haas. MMA and PDMS were purged with high-purity nitrogen before use in order to remove the oxygen.

Apparatus and Procedures. Gamma radiation-induced polymerization of MMA was carried out in a 43 cm^3 stainless steel high-pressure jacketed autoclave containing a magnetic stir bar and equipped with a Pt-100 temperature sensor, a pressure transducer, and a pressure gauge. The reactor, filled with the proper amount of monomer and surfactant, was deoxygenated by purging with nitrogen for 15 min and then charged at room temperature with the weighted amount of CO_2 by using an ISCO syringe pump; the initial pressure was about 60 bar. Irradiation was performed in the IGS-3 gamma irradiation facility, a panoramic 3000 Ci ^{60}Co irradiator, having an activity of 1200−1000 Ci during the period of the experiments. The investigated doses have been in the range 2.8−0.5 kGy, and the dose rates have been 4.9 and 8.6 Gy/min. The dose is the quantity generally sought in radiation chemical studies; it is the amount of energy absorbed per unit mass of irradiated material and is given in Joule per kilogram, which has the special name Gray (Gy). Reported values have been measured by using a PTW universal dosimeter. The temperature and pressure control during irradiation was ensured by a safety and control system based on a PI controller inserted in a cascade control loop. A schematic representation of the main components of the apparatus is shown in Figure 2.

At the end of the irradiation, the reactor was quenched in an ice−water bath, and the gas was bubbled immediately in cyclohexane in order to trap solid PMMA carried by the fluid. Finally, the reactor was opened, and the collected polymer was washed in cyclohexane in order to remove the unreacted monomer and surfactant, then recovered through filtration, and dried in a vacuum oven at 40 °C. Conversions were determined gravimetrically.

Table 1. Dispersion Polymerization of MMA in Dense CO_2[a]

dose, kGy	yield, %	$\langle M_n \rangle$, kg/mol	MWD	product	D_n[b]
T = 39 °C, Dose Rate = 8.6 Gy/min					
2.8	80	830	1.9	powder	3.4 (1.02)
2.0	55	530	2.4	powder	3.1 (1.01)
1.3	26	200	3.0	coalescent	
0.5	0.8	40	3.7	coalescent	
T = 30 °C, Dose Rate = 8.6 Gy/min					
2.8	81	670	2.1	powder	2.8 (1.09)
2.0	47	850	1.9	powder	2.4 (1.03)
1.3	25	152	3.2	coalescent	
0.5	2.6	34	3.6	coalescent	
T = 30 °C, Dose Rate 4.9 Gy/min					
2.6	92	560	2.5	powder	2.7 (1.1)
2.0	45	640	1.6	powder	2.3 (1.03)
1.6	24	575	1.5	powder	
0.5	2	45	2.0	coalescent	

[a] Reaction conditions: P = 60 bar when T = 30 °C and P ~ 77 bar when T = 39 °C. Reaction system: 9.5 g of MMA and 29 g of CO_2 in the presence of PDMS (5 wt % based on monomer). [b] Number-average diameter (in micrometers). The value in parentheses is the particle size distribution, PSD = D_w/D_n. Particle size is reported only when well-defined particles were obtained.

Polymer Characterization. Solubility tests on the synthesized polymer have been done in a Soxhlet extractor using THF close to its boiling point as a solvent with an extraction time of 48 h. Molecular weights of polymers were determined by GPC using a HP 1100 chemstation with two PLGel mixed columns in series, using THF as an eluent against PMMA standards (T = 35 °C, 1 mL/min flow rate, 20 μL injection, 0.1% w/v polymer solution), without correction for the presence of the branching in the polymer chains. Particle morphologies were analyzed and imaged with a Philips scanning electron microscope (SEM). Samples were sputter-coated with gold to a thickness of ~200 Å. The particle size distributions were evaluated by measuring 50−100 individual particles from the electron micrographs, and the number-average particle size and particle size distribution were determined.

Dynamic mechanical tests in the melt state were carried out with a RDA2 Rheometrics analyzer with plate and plate geometry (r = 12.5 mm), at 220 °C and 5% strain in the angular frequency range 10^{-1}−5 × 10^2 rad/s.

Results and Discussion

Effect of Radiation Parameters. Polymerization of MMA in liquid CO_2 at 30 °C, in the presence of PDMS−mMA macromonomer, using 2,2′-azobis(4-methoxy-2,4 dimethylvaleronitrile) (V-70) as initiator has been reported.[18] At the same temperature, and in the presence of the same macromonomer, PMMA has been obtained through gamma ray-induced radical polymerization. In Table 1, the experimental results obtained at the dose rate of 8.6 Gy/min, at increasing total dose, and 30 and 39 °C in the presence of 5 wt % surfactant are reported.

Because the dose rate can be considered constant during the experiment, the total dose and the corresponding time before the polymerization reaction starts account for the induction period. At both temperatures, the polymer yield varies linearly with the total dose (see Figure 3) up to very high conversion values. This is probably due to the combined effect of constant free-radical generation by γ-rays with the polymerization mechanism of the stabilized latex. Diffusion resistances of the monomer toward the growing macroradicals are overcome by the continuous generation of free radicals inside the micelles.

The average particle size (Figure 4) and molecular weight increase with the yield in a manner similar to

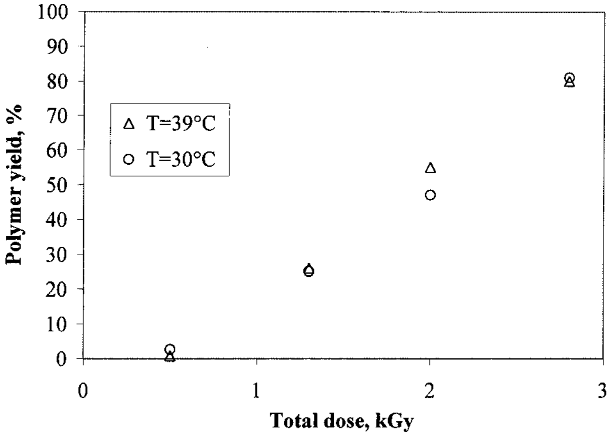


Figure 3. Effect of total dose on polymer yield for two different temperatures. Dose rate = 8.6 Gy/min. Reaction system: 9.5 g of MMA and 29 g of CO_2 in the presence of PDMS (5 wt % based on monomer).

reactions initiated by AIBN.[19] The polydispersity seems to decrease with an increase of the molecular weight. At low radiation doses with low conversion yields, the residual MMA present after the venting is able to dissolve the obtained polymer, so that undefined particles are recovered.

Table 2. Effect of Stabilizer Concentration[a]

stabilizer, %	yield, %	$\langle M_n \rangle$, kg/mol	MWD	product	D_n[b]
	40	120	3.4	coalescent	
2.5	70	690	2.1	powder	3.0 (1.04)
5	81	670	2.1	powder	2.9 (1.09)
10	78	660	2.4	powder	2.0 (1.01)

[a] Reaction conditions: dose rate = 8.6 Gy/min, total dose = 2.8 kGy, T = 30 °C, P = 60 bar. Reaction system: 9.5 g of MMA and 29 g of CO_2 in the presence of PDMS (5 wt % based on monomer). [b] Number-average diameter. See Table 1 footnote b.

The only influence of the temperature is on the average size of the particles. Under the hypothesis that the particle formation regime is completed at very low conversion values[20] and that the particle number remains essentially constant, with an increase in dimensions for the duration of polymerization, one suggestion is that, in the experimental conditions considered, the temperature increase affects the minimum coverage required to stabilize the surface area for the dispersion.

For what concerns the effect of the dose rate (see Table 1), apart from the expected increase of the polymerization rate, no significant differences in the molecular weight and particle size has been observed.

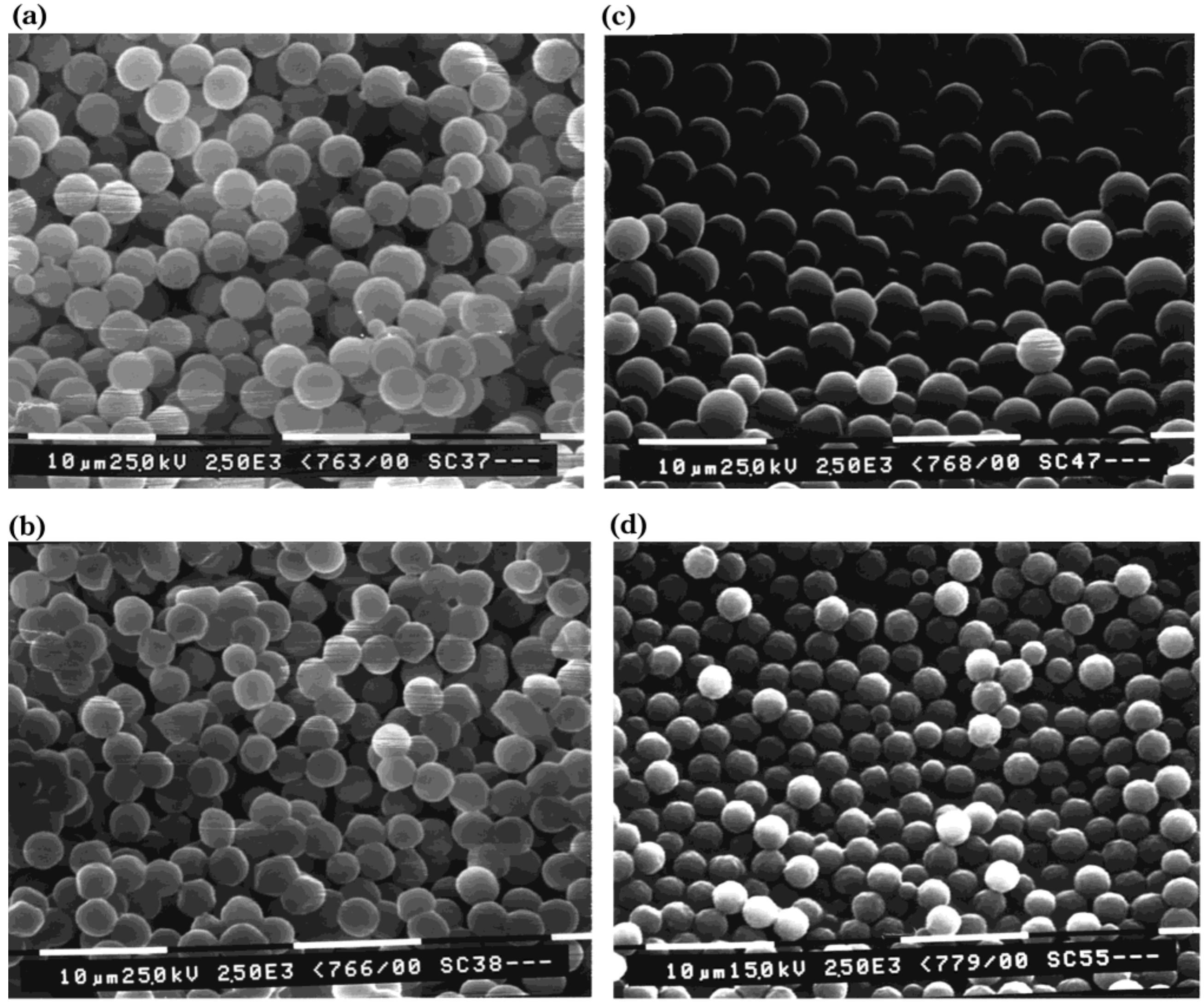


Figure 4. SEM micrographs of PMMA particles synthesized with a total dose of (a) 2.8 kGy at T = 39 °C, (b) 2.0 kGy at T = 39 °C, (c) 2.8 kGy at T = 30 °C, and (d) 2.0 kGy at T= 30 °C. All micrographs are at 2500X magnification.

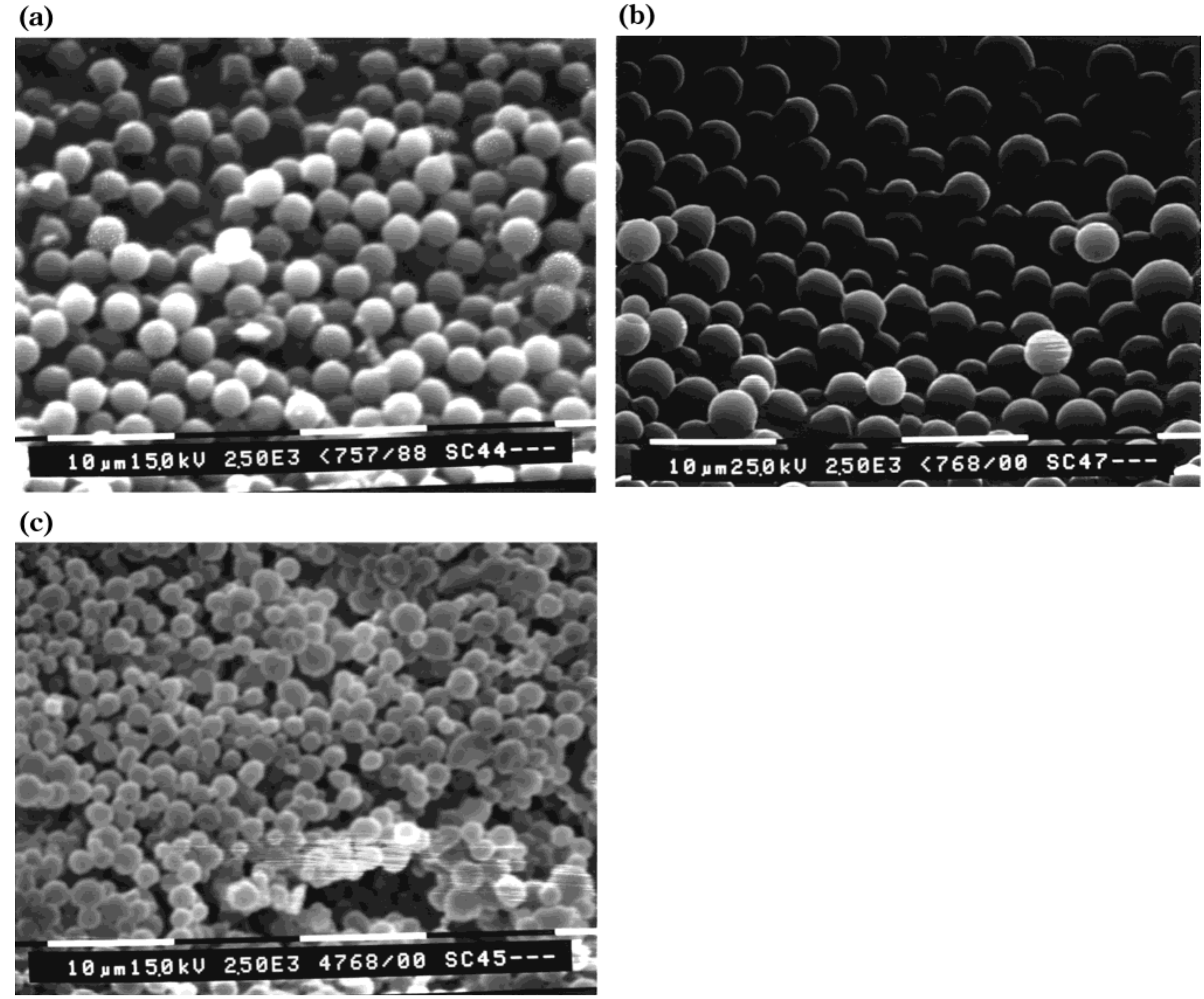


Figure 5. SEM micrographs of PMMA particles for dispersion polymerization carried out with (a) 2.5, (b) 5, and (c) 10 wt % PDMS macromonomer**.** All micrographs are 2500X magnification.

Table 3. Effect of Stabilizer Nature: Low-Molecular-Weight Stabilizers[a]

stabilizer	temp. °C	yield, %	D_n[b]	product	gel frac. %
V-Si2250 biacryloxy termin.	30	47	3.0 (1.05)	powder	>90
E-Si2330 biepoxy termin.	30	58	6.0 (1.01)	powder	<5
AMG006 biacetoxy termin.	30	24		hard sol.	<5

[a] Reaction conditions: total dose = 2.6 kGy, P = 60 bar, T = 30 °C, dose rate = 4.9 Gy/min. Reaction system: 9.5 g of MMA and 29 g of CO_2 in the presence of stabilizer (5 wt % based on monomer). [b] Number-average diameter. See Table 1 footnote b.

Effect of the Stabilizer Concentration. The effect of the PDMS−mMA macromonomer concentration is shown in Table 2. A low-yield and low-molecular-weight polymer without regular morphology is obtained in absence of stabilizer. According to the literature data,[18,20] the average particle size decreases as the concentration of the stabilizer increases (see Figure 5). The average particle size of PMMA obtained through γ-ray polymerization is lower with respect to that obtained in liquid CO_2 at the same temperature in the presence of V-70 initiator.[18]

Table 4. Effect of Stabilizer Nature: Stabilizers with 20 kg/mol Molecular Weight[a]

stabilizer	yield, %	D_n[b]	product
Sb1785 biacetoxy termin.	78	1.75 (bimodal distrib.)	hard solid/powder
Sb1784 biacryloxy termin.	88	2.37 (1.05)	powder

[a] Reaction conditions: total dose = 2.8 kGy, dose rate = 8.6 Gy/min, T = 30 °C, P = 60 bar. Reaction system: 9.5 g of MMA and 29 g of CO_2 in the presence of stabilizer (5 wt % based on monomer). [b] Number-average diameter. See Table 1 footnote b.

Effect of the Nature of the Stabilizer. A set of experiments have been carried out in the presence of bifunctional poly(dimethylsiloxane) surfactants at low (see Table 3) and high molecular weights (see Table 4). Biepoxy and biacryloxy stabilizers at low molecular weight and biacryloxy stabilizers at high molecular weight give rise to well-defined microspheres. The corresponding yields are in the range 50−90%. The acetoxy derivates (both high and low M_n) give rise to lower yields and poorly defined geometries with bimodal particle size distribution (Figure 6). Solubility tests indicated that all of the obtained polymers are soluble

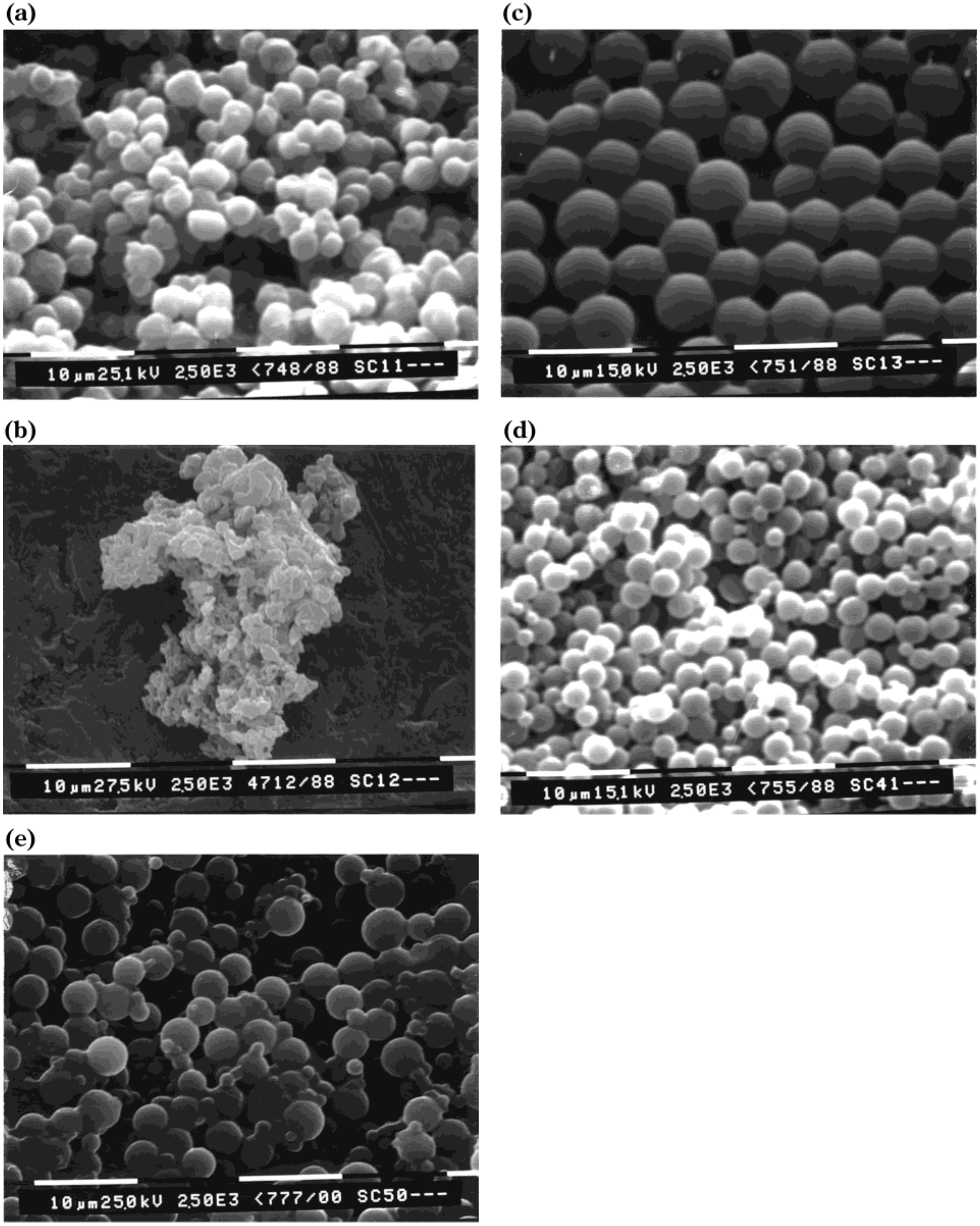


Figure 6. SEM micrographs of PMMA particles synthesized with different polysiloxane stabilizers: (a) Tegomer V-Si2250 biacryloxy-terminated, (b) Tegomer AMG006 biacetoxy-terminated, (c) Tegomer E-Si2350 biepoxy-terminated, (d) Tegomer Sb1784 biacryloxy-terminated, and (e) Tegomer Sb 1785 biacetoxy-terminated. All micrographs are 2500X magnification.

except for that obtained in the presence of the acryloxy low-molecular-weight surfactant.

Information about the influence of γ-ray-induced polymerization and of the stabilizer nature on the molecular structure of the polymers has been gained through dynamic mechanical analysis in the melt state. In Figure 7, flow curves for conventional PMMA and PMMA obtained both by γ-rays in bulk polymerization and in dense CO_2 without surfactants are reported. In Figure 8, analogous curves for PMMA obtained through γ-rays polymerization in the presence of some stabilizers are reported. It is possible to evidence that all flow curves relative to PMMA obtained through γ-rays are steeper than the flow curve for conventional PMMA. The presence of stabilizers enhances this behavior. It is well-known[21] that the lack of Newtonian regime is due to the typical complexity of polymer molecular structure, caused by high-molecular-weight, long-chain branching

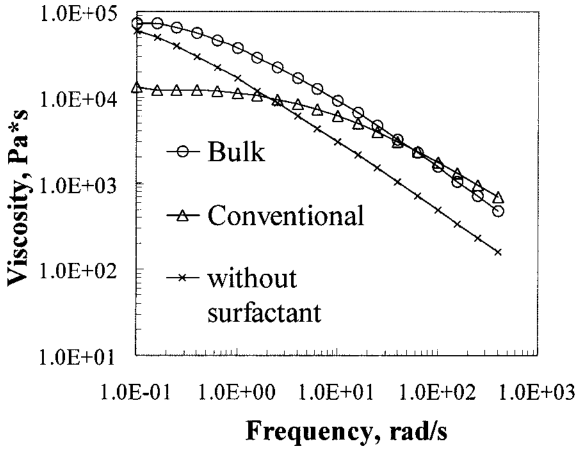


Figure 7. Flow curves of PMMA obtained by bulk polymerization with a total dose of 4 kGy (T = 70 °C), a conventional PMMA, and a polymer obtained in dense CO_2 without stabilizer at total dose of 2.0 kGy (T = 30 °C).

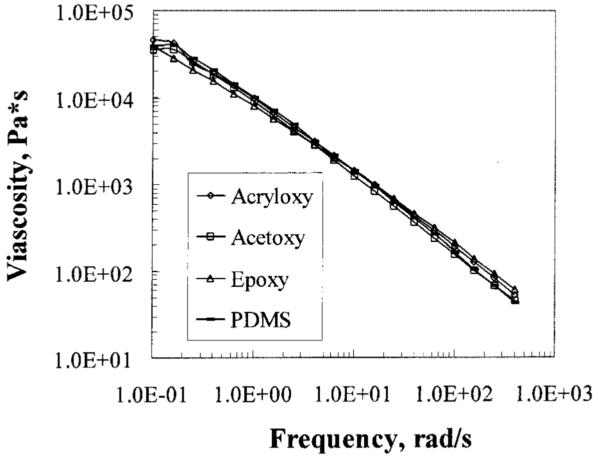


Figure 8. Flow curves of PMMA obtained with different stabilizers (V-Si2250, E-Si2330, AMG006, and PDMS−mMA, all with a concentration of 5 wt % with respect to the monomer). Reaction conditions: total dose = 2.0 kGy and T = 30 °C.

and cross-linking. The separate contributions can be drawn by more specific rheological measurements, such as very low-angular-frequency tests, or by other molecular investigations. In our case, solubility tests, reported in Table 3, and molecular weight determinations allow us to distinguish the cross-linking occurrence from the other two contributions.

Conclusions

The experiments up to now performed allow one to state that γ-rays are effective in the dispersion polymerization of MMA. The most relevant advantages of the initiation method lie in the possibility of both having a very pure starting system and operating in very mild temperature and pressure conditions. Moreover, γ-rays sustain the polymerization up to high conversions in short reaction times.

The choice of proper surfactants allows one to both obtain regular spherically shaped particles, with a very narrow particle size distribution, and influence the molecular architecture and the morphology of the polymer.

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