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Continuous Styrene - Methyl Methacrylate - Glycidyl Methacrylate Terpolymerizations in Homogeneous Mixtures with Supercritical Carbon Dioxide

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Summary: Free-radical terpolymerizations of styrene, methyl methacrylate, and glycidyl methacrylate were carried out in a tubular reactor in the presence of 20 wt.% CO_2 at temperatures between 120 and 180°C and pressures of 300 and 350 bar. The number average molecular weights, M_N, were mostly between 2000 and 3000 $g \cdot mol^{-1}$ and polydispersity indices around 2. In part of the experiments molecular weights were controlled by *n*-dodecyl mercaptan serving as the chain-transfer agent. PREDICI modeling indicates that the targeted molecular weights of M_N~2500 $g \cdot mol^{-1}$ and polydispersities around 2 may also be reached by using an initiator cocktail, a mixture of two initiators with significantly different decomposition rate coefficients. The predictions are confirmed experimentally.

Keywords: continuous polymerization; free-radical copolymerization; oligomers; supercritical CO_2

Introduction

Supercritical (sc) CO_2 has emerged as a promising reaction medium for chemical processes [1]. Particularly attractive features for application in polymerizations are the reduction of viscosity and the easy separation of $scCO_2$ from polymeric products. With the exception of some fluorinated monomers, the majority of polymerizations in $scCO_2$, so far were carried out in heterogeneous phase [2]. These reactions mostly require the use of stabilizers, which may remain in the final material and thus may affect product properties. Previously, we showed that low molecular weight polymers may be produced in solution of $scCO_2$ at close to complete monomer conversion in batch reactions [3]. $ScCO_2$ is also known to be a favorable process medium for particle generation, e.g. micronization of polymers may be achieved via the RESS (Rapid Expansion from Supercritical Solution) or the PGSS process (Particles from Gas Saturated Solutions) [1, 4]. Particular benefits of using $scCO_2$ as a reaction medium are expected with integral

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processes, in which the individual steps of polymer generation and particle formation, both in $scCO_2$, are combined. The production of powder coatings should be an excellent example of such an integral process.

In this contribution we report on the synthesis of styrene-methacrylate terpolymers in the presence of $scCO_2$ using a continuously operated tubular reactor set-up. These polymers have number average molecular weights, M_N, typically of 3000 $g{\cdot}mol^{-1}$. The reactions were carried out in homogeneous phase in order to avoid the use of stabilizers. Molecular weight control is achieved either by chain transfer to *n*-dodecyl mercaptan (DDM) or by the initiation rate.

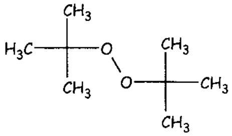
Experimental

Materials

Styrene (99%, Merck-Schuchardt), methyl methacrylate (MMA, 99 %, stabilized with 0.02 wt.-% hydroquinone, Fluka), glycidyl methacrylate (GMA, ≥ 97 %, stabilized with 0.005 % hydroquinone, Fluka), tetrahydrofuran (THF, Rotipuran ≥ 99.5%, p.a., stabilized with 2,6 di-*tert*-butyl-4-methylphenol, (Carl Roth), used as the eluent in size-exclusion chromatography (SEC) analysis), the chain-transfer agent *n*-dodecyl mercaptan (DDM, purum, ≥ 97 %, Fluka), and carbon dioxide (CO_2, grade 4.5, Messer Griesheim) were used as received. The following initiators were kindly provided by Akzo Nobel and were also used as supplied:

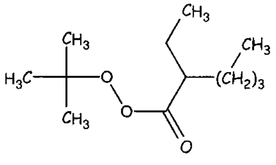
DTBP

di-*tert*-butyl peroxide



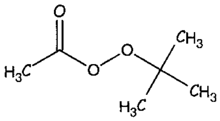
TBPO

tert-butyl peroxy-2-ethyl-hexanoate



TBPA

tert-butyl peroxyacetate



Tubular reactor set-up

The polymerizations in the presence of $scCO_2$ are performed in a tubular reactor. The experimental set-up is schematically shown in Figure 1. A pre-mixed solution of the monomers, the thermally decomposing initiator, and, if applied, the chain-transfer agent (CTA) are pressurized and pumped using an HPLC pump (Lewa MK-1). CO_2 is pressurized with a pneumatic HPLC pump built in the workshop of the Institute of Physical Chemistry. A constant CO_2 flow is established by means of an additional electric HPLC pump (Knauer K-1001). The monomers and additives together with CO_2 are fed into a dynamic mixing chamber (Knauer) to achieve a homogeneous reaction mixture, which is pumped through a tubular reactor of 8.5 m length and 3.8 mm internal diameter. The reactor is contained in an oil bath. At typical residence times of 22 minutes, laminar flow takes place [5]. Pressure is controlled by a combination of a ball and a needle valve (Swagelok). After passing the reactor, the mixture is depressurized and the polymer is collected. In order to prevent further polymerization, the polymer is precipitated with methanol. The dried polymer is analyzed by size-exclusion chromatography (SEC).

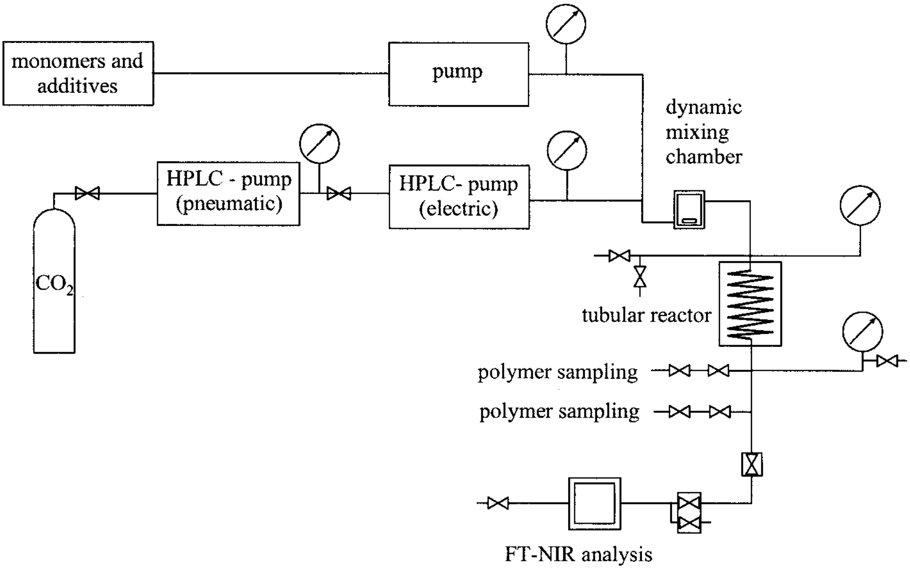


Figure 1: Scheme of the tubular reactor set-up. For details see text.

Analytical instrumentation

The initial monomer concentrations are measured via quantitative FT-NIR-spectroscopy in the region of the first overtones of the C-H stretching modes around 6170 cm^{-1} [6]. The spectra also allow for the determination of the CO_2 content. Molecular weight distributions (MWDs) are determined with an SEC set-up consisting of a Waters 515 pump, a Waters 410 refractive index detector, PSS-SDV columns with nominal pore size of 10^5, 10^3 and 10^2 Å, and tetrahydrofuran at 35°C as the eluent (flow rate 1 mL/min). Molecular weight calibration is established against narrow polydispersity polystyrene standards (MW = 410 to 2 000 000 $g{\cdot}mol^{-1}$) from Polymer Standards Service (PSS).

Results and Discussion

Batch polymerizations carried out at 120°C and 350 bar in the presence of DDM revealed that almost complete monomer conversion may be reached in homogeneous phase [3]. Based on these results, tubular reactor experiments were carried out. The temperatures were between 120 and 160°C and pressures between 300 to 350 bar. The initial monomer molar fractions, f_i, were always: $f_S = 0.07$, $f_{MMA} = 0.52$, and $f_{GMA} = 0.41$. The initial initiator (DTBP) concentrations were between 1 and 7 wt.%, and the initial DDM concentrations between 0.2 and 8 wt.%, with both these concentrations referring to the reaction mixture without taking CO_2 into account. The CO_2 content was around 20 wt.% for the entire set of experiments.

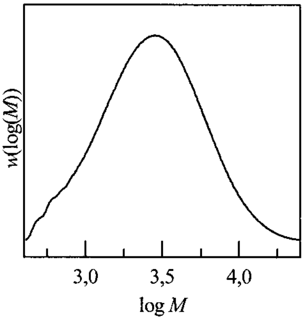


Figure 2: Molecular weight distribution of a styrene-MMA-GMA terpolymer from continuous polymerization in a tubular reactor at 160°C and 300 bar.

As an example, Figure 2 shows the molecular weight distribution for a terpolymer from a continuous experiment at 160°C and 350 bar using 5.5 wt.% DDM as the chain-transfer agent and 6.4 wt.% DTBP as the initiator. Residence time was 1320 s. The MWD is associated with an M_N of 2100 $g{\cdot}mol^{-1}$. The polydispersity is 1.8.

Additional experiments were carried out at 160°C and 350 bar. In a first experimental series, the initiator concentration was varied at DDM concentrations between 5.5 to 6.0 wt.%. The experimental details and the results are listed in Table 1. In all cases, polymers with $M_N = (2000 \pm 300)\ \mathrm{g \cdot mol^{-1}}$ and polydispersity indices ranging from 1.7 to 2.0 were obtained. The maximum conversions, x_{max}, accessible within the polymerizations were around 75-80 %.

c_{ini} /wt.%	c_{DDM} /wt.%	M_N /g·mol^{-1}	M_W / M_N	x_{max} / %
6.4	5.5	2100	1.8	75-80
6.4	5.5	1900	1.9	75-80
3.4	5.8	1900	1.8	75-80
3.4	5.8	2000	1.7	75-80
0.88	6.0	1800	2.0	75-80

Table 1: Reaction parameters and product properties (number average molecular weight, M_N, polydispersity index, M_W/M_N, final conversion, x_{max}) of terpolymerizations with $f_S = 0.07$, $f_{MMA} = 0.52$ and $f_{GMA} = 0.41$ carried out in a tubular reactor at 160°C, 300 bar and a CO_2 content of 20 wt.%.

In a second series of experiments, the DDM concentration was varied at initiator concentrations between 6.4 and 7.2 wt.%. The experimental details and the results are given in Table 2. A reduction in DDM concentration, from 6.0 to 0.17 wt.%, at almost constant DTBP concentration leads to a significant increase in M_N to 6900 g·mol^{-1} and to a higher polydispersity of 2.8. Even the relatively high initiator concentration of 7.2 wt.% is not sufficient to yield the targeted polymer molecular weights of around 2000 g·mol^{-1}.

c_{ini} /wt.%	c_{DDM} /wt.%	M_N /g·mol^{-1}	M_W / M_N	x_{max} / %
6.4	5.5	2100	1.8	75-80
6.4	5.5	1900	1.9	75-80
7.0	1.5	2900	1.9	75-80
7.0	0.67	5100	2.7	75-80
7.2	0.17	6900	2.8	75-80

Table 2: Reaction parameters and product properties (number average molecular weight, M_N, polydispersity index, M_W/M_N, final conversion, x_{max}) of terpolymerizations with $f_S = 0.07$, $f_{MMA} = 0.52$ and $f_{GMA} = 0.41$ carried out in a tubular reactor at 160°C, 300 bar and a CO_2 content of 20 wt.%.

Irrespective of initiator concentration, a maximum monomer conversion of around 80 % was reached. This limiting conversion is not due to dead-end polymerization, as x_{max} does not depend on c_{ini}. Moreover, at a residence time of 1320 s and a DTBP decomposition rate coefficient $k_d = 6.92\cdot10^{-4}\ \mathrm{s}^{-1}$ at 160°C, DTBP will not be entirely consumed at the reactor exit. It is suggested that the maximum conversion reached within the entire series of styrene-MMA-GMA terpolymerizations is determined by the reversibility of methacrylate propagation:

$$\mathrm{R}\cdot + \mathrm{M} \xrightleftharpoons[k_r]{k_p} \mathrm{R{-}M}\cdot$$

The activation energies of the associated propagation and depropagation rate coefficients of methacrylates are typically around $E_A(k_p) = 21\ \mathrm{kJ\cdot mol^{-1}}$ and $E_A(k_r) = 75\ \mathrm{kJ\cdot mol^{-1}}$, respectively [7]. Reverse propagation (depropagation) thus becomes dominant at high temperatures. For methacrylates, the depropagation reaction is negligible at temperatures up to 120°C [7]. At higher temperatures depropagation occurs, with the degree of depropagation being enhanced toward lower monomer concentration [8].

In order to estimate the influence of depropagation on x_{max}, polymerizations in bulk and in the presence of 20 wt. % of CO_2 were carried out at temperatures up to 180°C. The temperature dependence of x_{max} is shown in Figure 3. For MMA homopolymerizations in bulk, a reduction in x_{max} from almost complete monomer conversion at 120°C to 80 % at 180°C is seen. Addition of styrene ($f_S = 0.12$) to the reaction mixture increases x_{max}. This finding is explained by the fact that styrene does not depropagate at temperatures below 200°C [9]. It was suggested that, also within copolymeric radicals, styrene units disfavor depropagation [10]. Comparison of experimental data for styrene-MMA copolymerizations ($f_S = 0.12$) in bulk and in CO_2 demonstrates that lowering monomer concentration by the addition of this solvent results in a decrease of x_{max} at 160 and 180°C, x_{max} for reactions with 20 wt.% CO_2 being present is below the corresponding bulk polymerization value by about 13 % and 27 %, respectively.

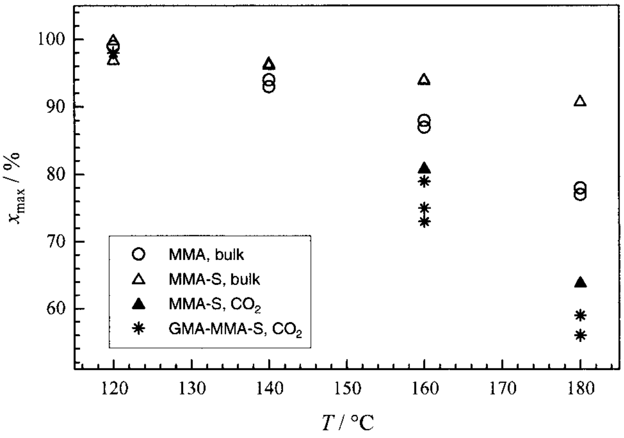


Figure 3: Maximum conversion, x_{max}, reached in MMA homopolymerizations in bulk, in MMA-styrene copolymerizations ($f_S = 0.12$) both in bulk and in 20 wt.% CO_2, and in GMA-MMA-styrene terpolymerizations in 20 wt.% CO_2.

Also presented in Figure 3 are results for terpolymerizations of styrene, MMA and GMA in CO_2 from experiments in the tubular reactor. x_{max} is reduced from almost 100 % at 120°C to around 60 % at 180°C.

The data in Tables 1 and 2 demonstrate that terpolymers with the same molecular weights and polydispersity indices as in batch may be produced in continuous experiments. With respect to technical applications, polymerization conditions however have to be modified. In particular, molecular weight control should be carried out with a CTA other than DDM, because of the odor of DDM and the relatively large DDM-derived fragment that is contained in the polymeric product. As an alternative, molecular weight may be controlled by initiation rate. In this case the reaction conditions have to be chosen such, that (i) the radical concentration is sufficiently high for effective MW control throughout the entire reaction and (ii) the initiator is consumed after the reaction. It was tested whether a mixture of two initiators, a so-called initiator cocktail, may provide a sufficiently large radical concentration throughout the entire reaction.

In order to identify suitable initiator cocktails, the decomposition rate coefficients of peroxides reported in the literature [11] were used to calculate initiator concentration vs. time profiles. As an example, Figure 4 illustrates initiator conversion as a function of time at 120°C (left) and at 160°C (right) for di-*tert*-butyl peroxide (DTBP), *tert*-butyl peroxy-2-ethylhexanoate (TBPO), and *tert*-butyl peroxyacetate (TBPA). At both temperatures, DTBP does not decompose completely within 1320 s, which is the typical residence time for the polymerizations carried out in the tubular reactor. On the other hand, TBPO has decomposed completely after a relatively short time interval at 160°C, whereas at 120°C around 95 % TBPO conversion is achieved after 1320 s. At 160°C, TBPA decomposes completely after around 700 s, whereas at 120°C less than 20 % of the initiator are decomposed within 1320 s.

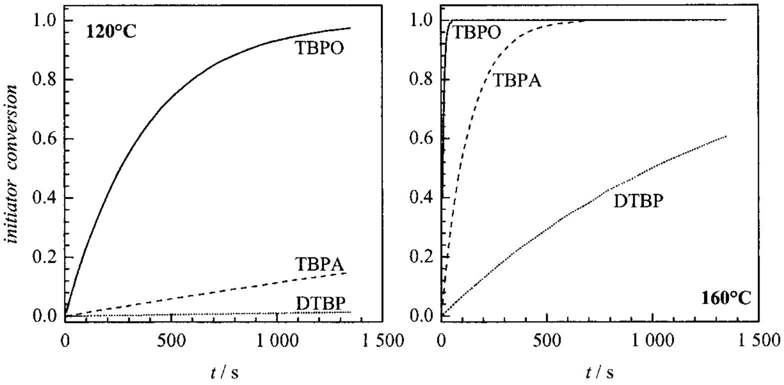


Figure 4: Initiator conversion vs. time profiles for DTBP, TBPO, and TBPA at 120°C and 160°C as calculated from literature decomposition rate coefficients [11].

The initiator conversion vs. time curves in Figure 4 indicate that none of the three initiators is perfect for effective molecular weight control during the entire course of the polymerization. Although no unreacted initiator will remain in the product obtained using TBPO or TBPA at 160°C, especially for TBPO initiated polymerizations molecular weight control may not be effective up to high monomer conversions. In cases where complete initiator consumption is reached at the end of the reactor (exemplified by the TBPO curve at 120°C), radical concentrations at the beginning of the polymerizations and thus high monomer concentrations will be too small for effectively controlling molecular weight. A similar situation would occur with TBPA at 140°C.

Because of the described issues associated with initiation by a single initiator, application of a mixture of two initiators is recommendable. This situation will be considered in the remainder of this Section. In order to identify suitable initiators and appropriate c_{ini} for this complex polymerization system, terpolymerization experiments were simulated using the program PREDICI [12]. Details of this modeling will be presented in an upcoming publication.

Figure 5 schematically illustrates simulation results for cocktails consisting of the initiators A and B. [13] The decomposition rate coefficient of initiator A, k_d(A), is two orders of magnitude higher than k_d(B). In Figure 5, the initiator derived radical concentration, c_R, and monomer conversion, x, are plotted as a function of reaction time. The diagram on the l.h.s. represents case (1) where equimolar amounts of initiator A and B have been applied. PREDICI simulation indicates that molecular weight control is effective and polydispersity of the product is low (close to 2). The kinetic situation underlying case (2) is such that the concentration of initiator B (r.h.s. plot in Figure 5) is only 10 % of the concentration of A. PREDICI simulation tells that in case 2 both molecular weight control and thus polydispersity are insufficient.

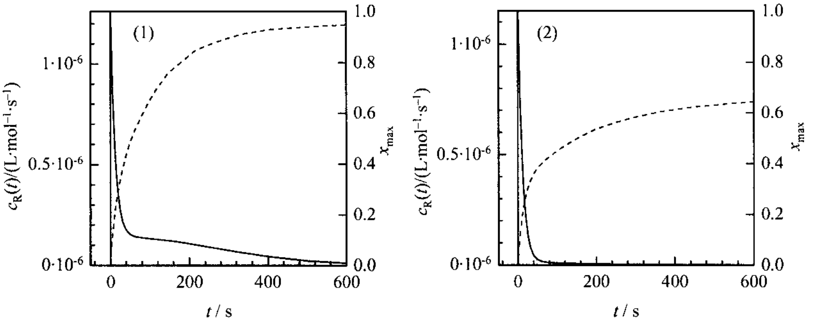


Figure 5: Initiator derived radical concentration (full line), c_R, and monomer conversion x (dashed line) as a function of time.

In cases 1 and 2, the initially very high radical concentration is due to the large concentration and a high decomposition rate coefficient k_d of initiator A. After relatively short time (t < 100 s) c_R is significantly decreased. In case 1, the remaining radical concentration is due to the decomposition of initiator B. With increasing time, c_R is further reduced, until at around 600 s radical concentration becomes very small. Under the condition of very low radical concentration, most of the monomer is already consumed. Thus the lack of molecular weight control by initiator derived radicals does not unfavorably affect MWD and polydispersity.

In case 2 the radical concentration is too small even after 100 s, where monomer conversion is far from being complete (see r.h.s. of Figure 5). The major differences in c_R and x_{max} vs. time result in favorable and in unfavorable molecular weight and polydispersity characteristics in cases (1) and (2), respectively.

Based on these modeling results a terpolymerization at 120°C and 300 bar was carried out in the tubular reactor set-up in the presence of 20 wt.% CO_2 with equimolar initial concentrations of initiator A and B. The polymer generated has a M_N of 3800 $g \cdot mol^{-1}$ and a polydispersity of 2.4. These values are already fairly close to the targeted values of $M_N = 2500\ g \cdot mol^{-1}$ and a polydispersity of 2.0.

Conclusions

Homogeneous phase styrene-MMA-GMA terpolymerizations may be carried out in a tubular reactor set-up up to high degrees of monomer conversion in the presence of $scCO_2$. The polymers obtained in the presence of DDM have low molecular weights in the range of $M_N = 2000\ g \cdot mol^{-1}$ and polydispersities mostly below 2.0. Modeling of the reactions allows for the identification of initiator cocktails, serving as an alternative to molecular weight control via the use of a chain-transfer agent such as DDM. Using two initiators provides sufficient radical concentrations over an extended time interval and thus allows for effective molecular weight control during the entire course of the polymerization reaction up to very high conversion.

Acknowledgements

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