Reversible Addition–Fragmentation Transfer Miniemulsion Polymerization of Styrene Induced by γ-Ray Irradiation

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(Received May 22, 2008; CL-080514)

Reversible addition–fragmentation transfer (RAFT) polymerization of styrene (St) induced by γ-ray irradiation has been successfully performed in miniemulsion using 2-phenylprop-2-yl phenyldithioacetate (PPPDTA) as chain-transfer agent (CTA). The results show that the polymerization bears all the characteristics of controlled/living free-radical polymerizations, such as the number-average molecular weight (M_n) increasing linearly with monomer conversion, molecular weight (MW) being controlled and the molecular weight distribution (MWD) being narrow (polydispersity index (PDI) $\leq$ 1.30). Moreover, this system does not show a significant decrease in polymerization rate as compared to a conventional miniemulsion polymerization.

Many efforts have been made to investigate living free-radical polymerization induced by γ-ray irradiation in bulk polymerization because of the advantages of radiation polymerization, such as relatively simply composed system, temperature independence, and strong penetrability, compared with chemical initiation.[1–3] The common drawback of all these processes is the very low polymerization rate which derives from the decreased concentration of propagating radicals. Moreover, bulk polymerization of St mediated either with CTA or without CTA can not be initiated by γ ray owing to the radiation protection of benzene ring. This problem can be overcome in principle by operating emulsion polymerization, so as to take advantage of radical segregation to decrease terminations without significantly reducing the polymerization rate with respect to the corresponding nonliving processes.[4]

A combination of the RAFT living mechanism, miniemulsion polymerization and γ-ray irradiation has been made in this work to achieve living characteristics without sacrificing the polymerization rate. To the best of our knowledge, this is the first report of RAFT miniemulsion polymerization of St induced by γ-ray irradiation.

The RAFT agent PPPDTA was synthesized using a method as reported.[5] St was purified by reduced pressure distillation prior to use. Sodium dodecyl sulfate (SDS) and hexadecane (HD) were used as emulsifier and costabilizer, respectively. The recipes for the miniemulsion polymerizations of St mediated both with and without PPPDTA are listed in Table 1.

The miniemulsion polymerizations of St are carried out under Co-60 γ-ray irradiation at a dose rate of 64.0 Gy/min for a prescribed time at room temperature.[11] The monomer conversions versus irradiation time are determined using gravimetry and are shown in Figure 1. The monomer conversion for both of the processes, as shown in Figure 1, reaches about 100% within 150 min. The slight decrease in the polymerization rate for Run 1 is probably due to desorption of the radical formed by the first exchange reaction of the RAFT agent in the polymer particles.[6] In particular, slow polymerization rates are associated with fast diffusing groups, while for highly water-insoluble groups (less prone to desorption) nonliving polymerization rates are obtained.[4]

Table 1. The recipes for the miniemulsion polymerizations of St induced by γ-ray irradiation mediated both with and without PPPDTA (dose rate = 64.0 Gy/min)

NO.	St/g	PPPDTA/g	SDS/g	HD/g	DDW/mL
Run 1	10	0.15	1.0	0.5	50
Run 2	10	0	1.0	0.5	50

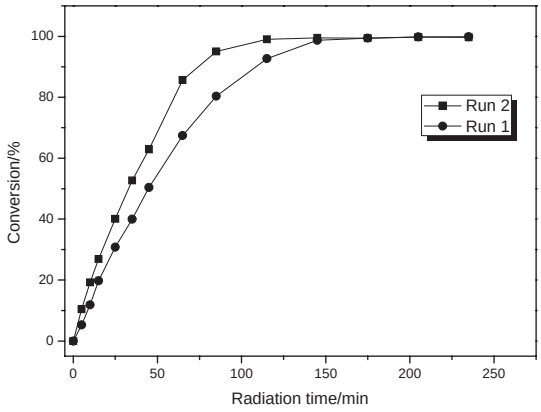

Figure 1. Monomer conversion versus radiation time for the miniemulsion polymerizations of St mediated both with (Run 1) and without PPPDTA (Run 2).

A given amount of the reaction mixture was taken out of the system at regular intervals, and then sodium chloride solution was added to precipitate the polymer. The pure PS was collected by filtration and dried in a vacuum oven at 40 °C. Gel permeation chromatography (GPC) (Waters Breeze) was used to investigate the M_n and PDI of PS.[11] The evolution of M_n and PDI of PS with monomer conversion is shown in Figure 2. It is seen that a good control of the polymerization was achieved, as indicated by the linear growth of M_n with conversion and by the low MWD values (PDI $\leq$ 1.30).

Relatively poor results in terms of polydispersity are usually observed in RAFT miniemulsion polymerization initiated by chemical initiator. These results are always ascribed to a nonuniform concentration of the dormant chains, arising from the dif-

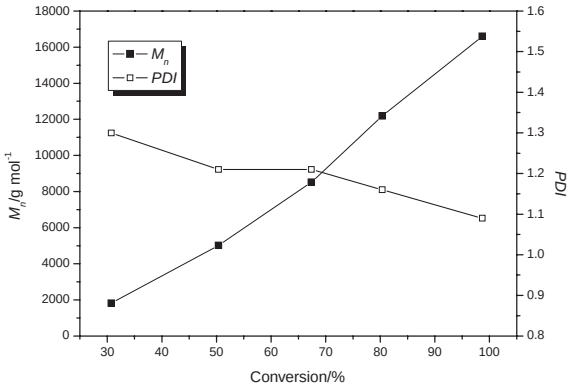

Figure 2. Evolution of MW and MWD of PS with monomer conversion for the RAFT miniemulsion polymerization of St induced by γ-ray irradiation.

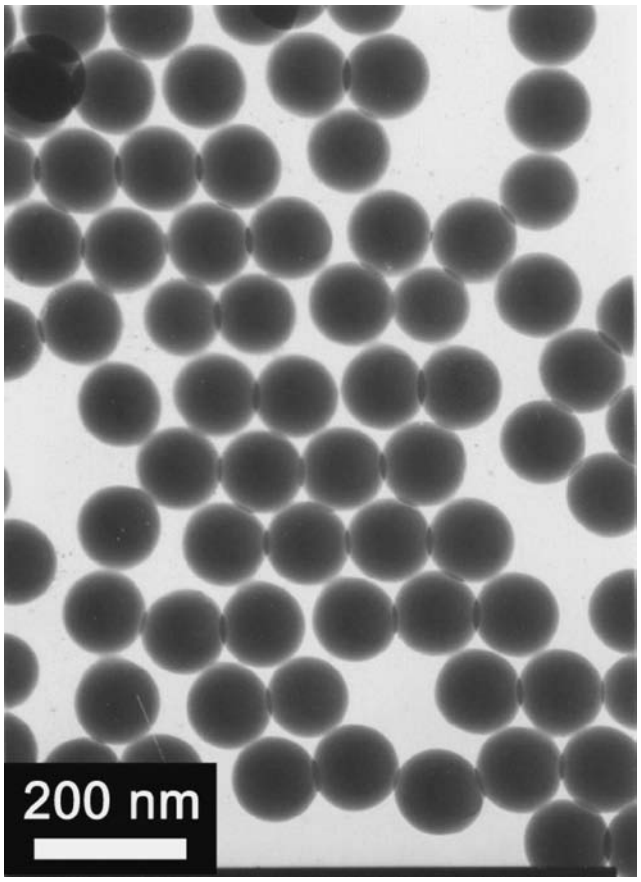

Figure 3. TEM images of PS latex particles for the RAFT miniemulison polymerization of St induced by γ-ray irradiation (conversion = 98%).

ferent reactivity of the different particles already mentioned in the case of St.[7–9] However, the polydispersity of obtained PS in this work is never higher than even 1.30 in a large range of monomer conversion from 30 to 99%. The reason for this phenomenon is still not clear. However, the special initiation method, γ-ray irradiation, is probably responsible for the narrow molecular weight distribution.

Transform electron microscopy (TEM) is used to investigate the morphology of the final PS latex particle (98% conversion).

As shown in Figure 3, most of the latex particles present in perfect spherical shape, and the average particle diameter calculated based on the report[10] is about 110 nm. Furthermore, the particle size distribution is very narrow (PDI = 1.06).

RAFT miniemulsion polymerization of St mediated by PPPDTA has been successfully carried out with a Co-60 γ-ray source. The results, such as linear relationship between molecular weight and monomer conversion, controlled molecular weight and narrow molecular weight distribution, suggested that the miniemulsion polymerization of St induced by γ-ray irradiation is a living free-radical process in the presence of PPPDTA. It should be noticed that the achievement of living characteristics does not sacrifice the polymerization rate with respect to the corresponding nonliving processes.

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11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) July 5, 2008; doi:10.1246/cl.2008.850