

Synthesis of Polypropylene-Polystyrene Copolymer via Ultrasonic Irradiation-Initiated Polymerization of Styrene in Polypropylene Solution

Hyungsu Kim*, Jihye Kim, and Miwha Kim

Applied Rheology Center, Department of Chemical Engineering, Dankook University, Seoul 140-714, Korea

Seyoung Oh and Jaewook Lee

Applied Rheology Center, Department of Chemical Engineering, Sogang University, Seoul 121-742, Korea

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Abstract : Polystyrenes(PS) were grafted onto polypropylene(PP) in the PP solution by ultrasonic irradiation-initiated polymerization of styrene. The resulting products consisted of mixtures of homopolymers and PP-PS copolymer because of the homopolymerization of styrene itself and copolymerization with PP. The dependency of the designated polymerization on sonication times was investigated to monitor the evolution of the copolymerization. Formation of the PP-PS copolymer was confirmed by FTIR analysis of the reaction products after a proper separation procedure of free PS and PP-PS copolymer. It was found that the tendency for the formation of PP-PS copolymer was closely related with the phase behavior of the PP/styrene mixture which was also influenced by sonication time. In order to verify the effectiveness of the PP-PS copolymer as a compatibilizer for PP/PS blend, melt mixing of PP/PS/PP-PS was performed in a batch mixer. During the mixing, the average torque was higher for the blend containing PP-PS copolymer influencing compatibilization. In accordance with the results from FTIR analysis and torque measurement, the PS domain size remarkably decreased in the PP/PS/PP-PS blend.

Introduction

Studies on ultrasound-assisted chemical reactions were started from 1950's.¹ Concerning various benefits of higher yield, enantioselectivity, purity, and reaction rate, the ultrasound-assisted reaction has been a promising approach in the area of modification of the existing novel materials.² There are numerous aspects on the nature of the chemical reactivity generated under ultrasonic irradiation (or sonication). Whatever the precise origin of chemical effects, it is generally recognized that sonochemical reactions in liquid proceed by cavitation collapse of a bubble. Upon the collapse of a bubble, the local temperature is increased up to 5,000 °C, which enables decomposition of molecules and then lead to the production of excited states, bond breakages, and the forma-

tion of free radicals. By this reason, the bubbles are recognized as microfurnaces and the model is called 'hot spot' theory.³ In this model, only a few molecules in a hot spot can be decomposed and the subsequent quenching is very efficient because the bubbles are so small compared to the volume of surrounding liquid.

Along with the synthesis of low molecular mass compounds, applications of the sonochemical effects in polymer system have yielded a variety of useful consequences, although relatively little attention has been given in this area. For example, ultrasound was used as an initiator in radical polymerization of vinyl monomers. The majority of studies have concerned with the homopolymerization in bulk^{4,8} or solution system.⁹⁻¹¹ Another area of the applications involves degradation of polymer molecules in solution.¹² When macromolecules are under sonication in liquid phase, they are subject to shock waves emanated from the collapse of the

*e-mail : hkim@dankook.ac.kr

cavities. On the molecular level, this implies a rapid motion of solvent molecules to which the macromolecules embedded in the solvent cannot follow. At such condition, friction is generated which causes strain and eventually bond rupture in the macromolecules. Thus, the primary product of the sonochemical cleavage of polymer chains is a macromolecular radical (or macroradical). Besides the effect of controlled degradation, one important aspect of this process is the possibility that macroradicals can act as active sites for further reaction with other monomers or polymers. By this means, it becomes possible to build block or graft type copolymers in a relatively simple manner compared to conventional polymerization techniques such as anionic polymerization, as demonstrated by a number of workers.^{13,14}

In this study, an attempt has been made to produce PP-PS copolymer via ultrasonic irradiation in the mixtures of polypropylene (PP) and styrene monomer (SM). The copolymer of PP and PS may be industrially useful for the compatibilization of the corresponding blends by various reasons. In fact, due to the importance of this type of copolymer, living radical graft polymerization of styrene to PP has been carried out under specially designed reaction scheme, where PP radicals were generated by irradiation in air.¹⁵ Compared to other studies, the present work was performed in a relatively simple manner without any chemical initiators or catalysts. Sonication times were changed to investigate the evolution of the designated polymerization process. In addition, the performance of the PP-PS copolymer as a compatibilizer was assessed in the blend of PP/PS.

Experimental

Materials. PP (powder) used in this study was a commercial product made by Daelim Industrial Co. of Korea with a melt index of 820 (230 °C, 2.16 kg). PS was provided by Cheil Industries, Inc. of Korea under the trade name of Starex HR-2390. The number average molecular weight (M_n) of the PS was about 70,000 with a polydispersity of 3.4. SM (Kanto Chemical) was washed with 10% NaOH three times to remove the inhibitor before being distilled under reduced pressure.

Sonication Procedure. Mixtures of PP and styrene were irradiated in a probe batch reactor. A horn type ultrasonic homogenizer (Sonics & Materials, Inc., VCX 600) equipped with a titanium tip with 1/2" in diameter was used. The homogenizer was operated at 450 W by using 20 kHz of ultrasound in a pulse ratio of 5:5. The pulse ratio designates on/off ratio of sonication time in seconds and the 'off' time allows the system to cool between the pulses of sonication. The maximum sonication time was limited within 50 min to prevent overheating of the probe. The amount of PP was fixed at 10 g in 200 mL of styrene. The polymerization was started at 20 °C unless otherwise mentioned and the temperature was measured with a thermocouple throughout the reaction. In order to trace the progress of the polymerization process along with the temperature variation, the reaction was proceeded without temperature control. Unlike other typical polymerization reactions, we did not purge the reaction mixture with nitrogen or argon gas, since oxygen is found to be capable of adding a SM to regenerate a normal chain radical.¹⁶ However, the separate influence of oxygen on polymerization was not observed in this study. Before subsequent experiments, all the polymerized samples were dried in a vacuum oven at 70 °C overnight.

Measurements. In order to assure the formation of the PP-PS copolymer, the reaction products were put into a proper separation procedure, by which PS homopolymer (or free PS) and PP-PS copolymer were separated. After the reaction, the samples were immersed into THF and filtered in order to extract the free PS. The free PS was precipitated from THF solution into methanol, and dried in a vacuum oven at 70 °C for 24 hrs. The sample of PP-PS copolymer was washed by a Soxhlet extraction with THF for 12 hrs and dried in a vacuum oven at 70 °C for 24 hrs. The existence of PS units grafted to PP chains was investigated by Fourier transform infrared spectroscopy (FTIR, Shimadzu 8501). The M_n of free PS was measured by GPC (Waters 410). Scanning electron microscopy (SEM, Jeol, JSM 5800) was used to observe the phase size in various blends considered in this study.

Melt Mixing. Melt mixing of blends based on

PP, PS and the reaction product made in this study were performed in an intensive mixer (Haake Rheomix 600). Each blend was prepared on a fixed volume basis of 80% and loaded at 200 °C. The rotor speed was set as 120 rpm and the mixing time was 10 min.

Results and Discussion

Figure 1 describes the temperature variations in the mixture containing 10 g of PP during the sonication of 50 min. From the beginning of the experiment, the temperature is continuously raised up to a temperature of 130 °C. The observed level of the reaction temperature is lower than that obtained by a simple calculation based on the data of heat of polymerization and specific heat of styrene.¹⁷ For the reaction volume of 200 mL of SM the attainable increase of temperature upon complete conversion is nearly 400 °C at adiabatic condition, as is typically experienced in free radical polymerization in bulk state. Also additional increase of the temperature is provoked by ultrasonic energy. In the present case, of course, the less increase in the reaction temperature is due to the incomplete conversion of styrene monomers and heat transfer to the surroundings. However, further heat dissipation is inevitable to achieve homogenization of the reaction mixture which is followed by complete mixing between the components. For the effective dispersion of PP in styrene

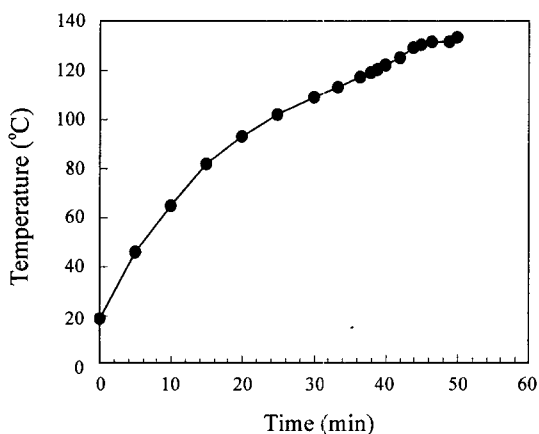


Figure 1. Temperature variation versus sonication time (PP = 10 g).

matrix, enough energy should be available to heat the surface of PP powders and to overcome the enthalpy of fusion. In other words, PP powders may act as a heat sink of the system. Although the homogeneity of the reaction mixture is improved by the action of the ultrasonic wave, perfect mixing is hardly guaranteed unless favorable interactions between the two exist. This issue is relevant to the phase behavior of PP/styrene system, and it is important to note that there was a significant transition in the turbidity of the mixture during the polymerization. At the beginning of sonication, the PP powders were suspended in styrene matrix. After the continuous sonication and increase of the reaction temperature, however, the mixture became transparent around the temperature of 121 °C, showing miscibility of PP with styrene at the elevated temperature. And then, the appearance of system was changed into opaque along with the subsequent polymerization. Although careful study on the phase behavior of PP/styrene should be preceded, it is reasonable to expect such behavior since the solubility parameters of PP and styrene are reported as 18.8 and 19.0 (MPa^{1/2}, at 25 °C), respectively.¹⁸ Moreover, it is interesting to note that a similar phase behavior was observed in a study on the living radical polymerization of PP with styrene at a temperature of 125 °C, where the reaction system in the early stage was homogeneous but in the final stage seemed to be inhomogeneous.¹⁵ The miscibility of PP and styrene is of paramount importance in promoting the intended copolymerization without extra solvents; and we believe that the existence of phase transition is closely related with the growing population of high molecular weight PS chains and the onset of copolymer formation simply because grafting or blockcopolymer formation is not feasible unless the system is properly homogenized in the molecular level. In fact, in a polymerization conducted at a constant temperature of 60 °C, no phase transition was observed and the viscosity of the reaction medium was relatively low.

As previously described, collapse of bubble in styrene phase induces flow fields of high velocity gradient, i.e. inhomogeneous flow of the monomer molecules. If a PP chain is located in a region of a high velocity gradient and if it is sufficiently

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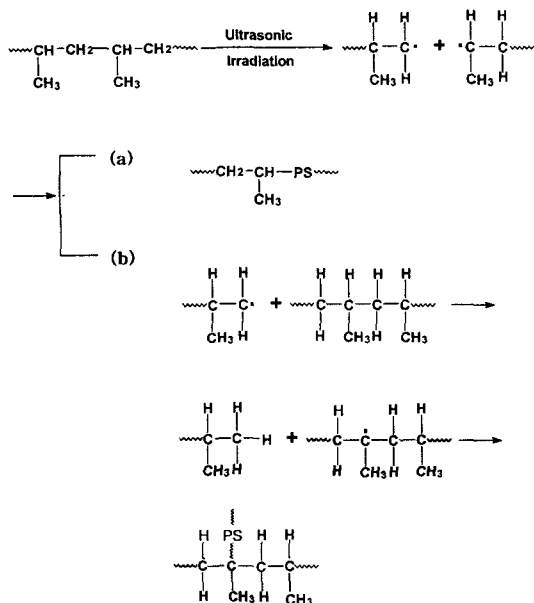


Figure 2. Depiction of possible routes for copolymer formation. (a) Block copolymer formation by main chain scission of PP and (b) graft copolymer formation by H abstraction of PP.

strained, chain fractures become feasible and thus macroradicals of PP having the active site in the chain end are formed. On the other hand, different type of PP macroradicals may also be generated by chain transfer reactions from growing chain radicals of styrene or from other PP macroradicals, where the hydrogen atoms of PP molecules are abstracted and the active sites are left within the main chain. Depending on the source of the radicals, either block or graft copolymers of PP and PS can be made by the polymerization of styrene on the active sites of PP macroradicals or direct combination of PP and PS macroradicals. A simplified description for the various possible mechanisms is given in Figure 2. Although exact distinction for the types of the copolymers is not available, an evidence for the copolymer formation was found in the FTIR analysis of samples prepared by removing free PS from the reaction products. As shown in Figure 3, the CH bending vibration of a PS benzene ring appeared at 700 cm^{-1} , which confirms the existence of PS component grafted to PP chains.¹⁵ Based on the peaks found from the FTIR analysis and a calibration curve obtained from the

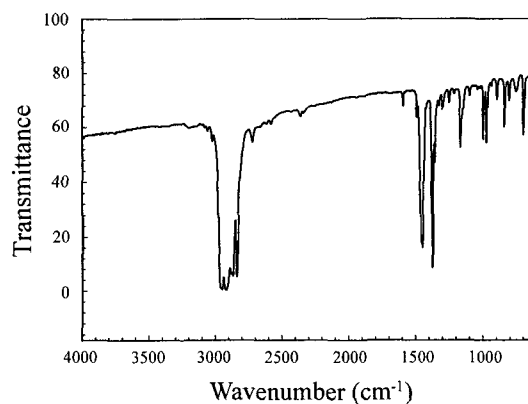


Figure 3. FTIR spectra of reaction products without free PS (50 min sonication).

Table I. Effect of Sonication Time on the Graft Ratio (Wt. of PS/Wt. of PP)

Time(min)	Graft Ratio
40	0.3
45	2.7
50	2.8

blends of PP/PS with known compositions, graft ratios, defined as the weight ratio of the graft PS to PP, were calculated. The ratio of the IR absorbance of the PS(700 cm^{-1}) to that of PP(810 cm^{-1}), where the absorption of 810 cm^{-1} is assigned to the CH₂ and CH rocking vibration of the PP, was used for each calculation. As summarized in Table I, there was a significant increase in the graft ratio after the onset of homogeneity in the system, which was observed around 40 min of sonication. The trend found here is closely related to the issue on the phase behavior of PP/styrene, viz., complete mixing is the prerequisite for the copolymerization, as discussed previously.

Although the major focus of the present work is to generate PP-PS copolymer, homopolymerization of PS should, in principle, constitute an important part of the overall reaction. Thus, in order to explore the evolution of the specified polymerization in detail, M_n of PS(free PS) was measured and plotted as a function of sonication time in Figure 4. It appears that within the available samplings for various reaction periods, the average molecular weight increases with sonication time

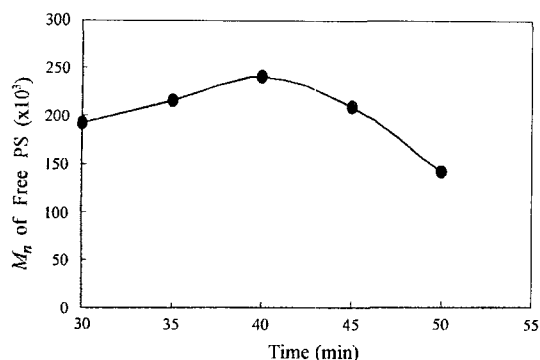


Figure 4. Effect of sonication time on the M_n of free PS.

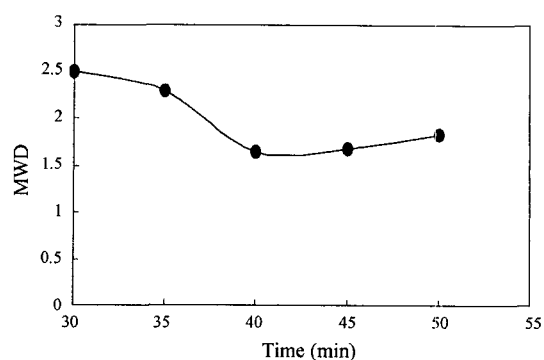


Figure 5. Effect of sonication time on the molecular weight distribution (MWD) of free PS.

from 30 to 40 min, and then starts to decrease until the end of sonication. This implies that a maximum level of the molecular weight exists when the reaction temperature is continuously raised. Consequently, the result shown in Figure 4 is somewhat different from the case of conventional free radical polymerization of styrene, where the molecular weight is supposed to decrease as the temperature increases. Of course, the exact interpretation for the above results is not readily available due to the dynamic nature of the present system including undetermined rate constants and varying monomer concentration throughout the reaction process. Nevertheless, a plausible explanation is given by the interplay of ultrasonic degradation and thermal effect. As the temperature decreases (from right to left in the time axis of Figure 4), the variation of the molecular weight is in accordance with that of typical free radical polymerization; however, as the temperature is further decreased, the propensity for violent cavitation and subsequent chain breakage of constituent polymers is intensified due to the lower vapor pressure of the liquid.⁸ Thus, a maximum molecular weight is obtained during the sonication between 30 and 50 min. A relevant issue is also pertinent to the minimum value of molecular weight distribution around 40 min of sonication (Figure 5).

Additional evidences for the copolymer formation were available from the torque measurement during melt mixing and subsequent observation of phase size in SEM. For the necessary comparisons, the reaction product (designated as PP-g-PS)

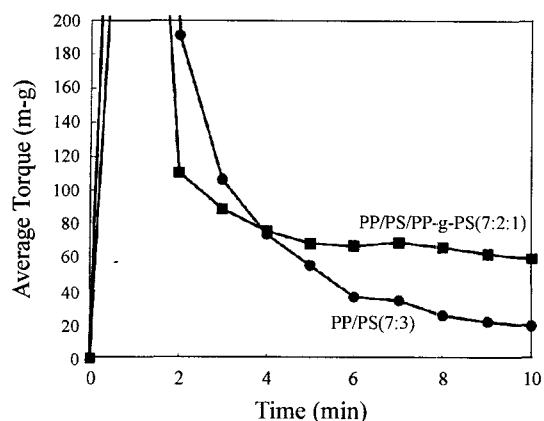


Figure 6. Effect of PP-g-PS on the average torque of PP/PS blend during melt mixing.

obtained by 50 min of sonication with 10 g of PP was added to the blend of PP/PS(7:3) in 10 wt%. When the PP-g-PS was incorporated, the average torque was higher than that of the simple binary blend of PP and PS (Figure 6). Furthermore, it is shown in Figure 7 that the domain size of PS was remarkably reduced by adding PP-g-PS. Although the increased torque may be partially due to the higher molecular weight of PS in PP-g-PS than that of the PS in binary blend, these results manifest the role of PP-g-PS as a compatibilizer for immiscible blend of PP/PS. Accordingly, the designated copolymers would be preferentially located at the interface between the component polymers, by which enhanced entanglements between the component polymers are promoted and the interfacial tension is reduced.

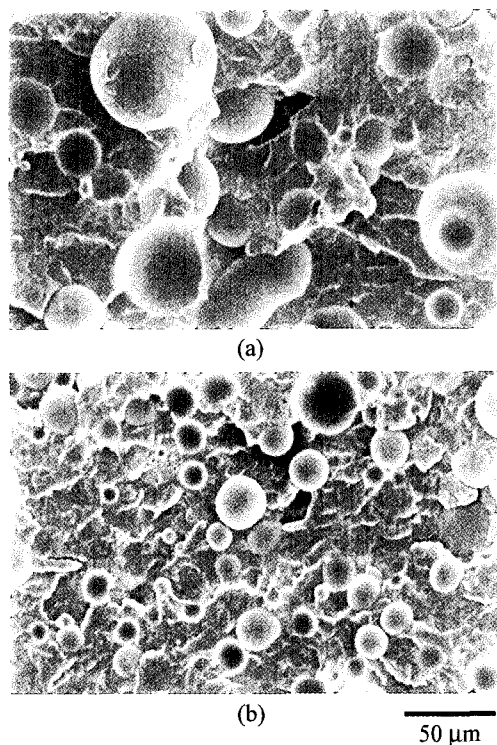


Figure 7. SEM photomicrographs of (a) PP/PS(7:3) and (b) PP/PS/PP-g-PS (7:2:1).

Conclusions

Polymerization of SM was conducted in the presence of PP by using ultrasonic irradiation. The expected roles of the ultrasonic wave were to generate radical species of styrene and to induce chain scission of PP molecules, by which both homopolymerization of PS and copolymerization with PP were accompanied. Based on the various results and observations found in this study, a plausible mechanism of the polymerization is proposed as follows. At the early stage of the sonication, homopolymerization of PS prevails; however, as the reaction continues, PP powders are completely dissolved in styrene matrix owing to the heat evolved during the sonication and polymerization of styrene. An important issue that enters the picture here is the miscibility of PP/styrene at the elevated temperature, which enables uniform dispersion of PP molecules and subsequent chain scission of them. In this manner, macroradicals of

PP are generated and the proposed copolymerization is accomplished.

Regarding the types of the copolymers formed by ultrasonic irradiation, it is possible to expect the formation of block copolymers in case of chain cleavage, while graft copolymers are made in the other cases. A rather simplified system attempted in this study may be optimized to modify existing polymers to impart various useful functions in a systematic manner.

Future work needs to focus in more detail on the quantitative analysis for the evolution of the copolymerization process. More diversified approaches are in progress for various reaction temperatures with different monomers. Finally, there is a strong impetus for applying current system in developing thermoplastic nanocomposites. According to the unique action of ultrasonic wave, nanoscale dispersion of silicate layers is readily achieved.¹⁹

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