

Radical Polymerization of Vinyl Monomers in the Presence of Carbon Black Initiated by 2,2'-Azobisisobutyronitrile and Benzoyl Peroxide in Ionic Liquid

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ABSTRACT: The radical polymerization behavior of vinyl monomers, such as styrene, methyl methacrylate (MMA), and vinyl acetate (VAc), in the presence of carbon black initiated by benzoyl peroxide (BPO) and 2,2'-azobisisobutyronitrile (AIBN) in ionic liquid (IL) was compared with those in toluene. 1-Butyl-3-methylimidazolium hexafluorophosphate was used as IL. The radical polymerization of vinyl monomers initiated by BPO and AIBN in the presence of carbon black was remarkably retarded in toluene. On the contrary, the retardation of the polymerization by carbon black was considerably reduced in IL. During the radical polymerization in the presence of carbon black, a part of polymer formed was grafted onto carbon black

surface based on the termination reaction of the growing polymer radicals with carbon black surface. The percentage of grafting and molecular weight of polymer in IL were much higher than those in toluene. This may be due to the fact that lifetime of the growing polymer radical is prolonged because of high viscosity of IL. Therefore, the growing polymer radicals with higher molecular weight were trapped by carbon black surface, because of stabilization of polymer radicals. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3300–3305, 2008

Key words: radical polymerization; initiators; graft copolymers; ionic liquid; surface grafting

INTRODUCTION

It is well known that carbon blacks act as a strong radical scavenger. It has been reported that the reactivity of methyl radicals to polycondensed aromatic compounds increases with increasing number of aromatic rings.¹ For example, the reactivity of methyl radicals to carbon black is 10^7 times of benzene.^{2,3}

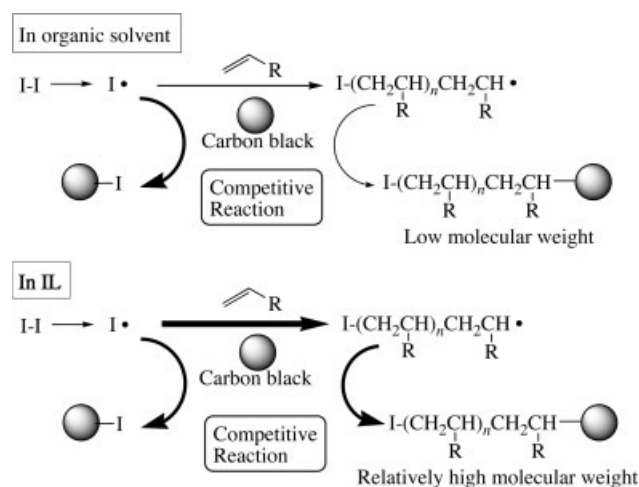
Therefore, the competitive reaction of growing polymer radicals and primary radicals, formed by the thermal decomposition of initiator, against carbon black surface proceeds during radical polymerization in the presence of carbon black as shown in Scheme 1. For example, the radical polymerization of vinyl monomers with negative e -value initiated by benzoyl peroxide (BPO) was remarkably retarded, but that with positive e -value was inhibited. On the contrary, when 2,2'-azobisisobutyronitrile (AIBN) was used, carbon black acts as moderate inhibitor and retarder of the polymerization of vinyl mono-

mers with positive and negative e -values, respectively.^{4–6} During the polymerization, a part of polymer formed was grafted onto carbon black surface based on the trapping of growing polymer radicals as shown in Scheme 1. However, the percentage of grafting in organic solvent was less than 10%, because of preferential trapping of low molecular weight initiating radicals (Scheme 1).^{4–6}

If the competitive reaction of initiating radicals and growing polymer radicals against carbon black surface can be controlled, polymer-grafted carbon black with higher percentage of grafting will be obtained. We have pointed out that polymer radicals formed by the decomposition of macro azo-initiator and azopolymer, and thermal dissociation of 2,2,6,6-tetramethylpiperidyl-1-oxy (TEMPO)-terminated polystyrene were successfully trapped by carbon black surface to give the corresponding polymer-grafted carbon black with higher percentage of grafting, because of the absence of low molecular weight radicals.^{7,8}

Recently, organic synthesis and polymerization in ionic liquids (ILs) as a reaction solvent has been reported. ILs are nonvolatile, nonflammable, and thermally stable solvents.^{9–11} These properties promise replacements for the traditional volatile organic

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Scheme 1 Competitive reaction of initiator radical and growing polymer radical onto carbon black surface in organic solvent and in IL.

solvents. Therefore, the number of studies on ILs as reaction media has increased markedly.

For example, the polymerization of methyl methacrylate initiated by photo initiator at 25°C¹² and 2,2'-azobisisobutyronitrile at 70°C¹³ in IL has been reported. The rate of the radical polymerization and molecular weight of polymer in IL were much larger than those in benzene.^{12,13} The atom transfer radical polymerizations in IL were recently reported by many researchers.¹⁴⁻¹⁷

In the preceding paper, we have reported the effect of IL on the radical graft polymerization of vinyl monomers onto silica nanoparticle and carbon black initiated by azo groups previously introduced onto the surface.¹⁸ It became apparent that the rate of polymerization and percentage of grafting were much larger than those in organic solvents.

In this work, the radical graft polymerization of vinyl monomers initiated by BPO and AIBN in the presence of carbon black in IL was investigated. The effects of IL on the competitive reactions of initiator radicals and growing polymer radicals against carbon black surface will be discussed.

EXPERIMENTAL

Materials and reagents

Carbon black used was channel black (commercial code, FW 200) obtained from Degussa A.G. The specific surface area and average particle size were 460 m²/g and 13 nm, respectively. The content of phenolic hydroxyl and carboxyl group was determined to be 0.10 and 0.61 mmol/g, respectively. The content of phenolic hydroxyl and carboxyl groups on the surface was determined by use of *N,N*-diphenyl-1-picrylhydrazyl¹⁹ and NaHCO₃,²⁰ respectively. The carbon black was dried *in vacuo* at 100°C before use.

Styrene obtained from Kanto Chemical, Japan was washed with 10% aqueous solution of sodium hydroxide and water, dried over calcium chloride, and distilled before use. Methyl methacrylate (MMA) obtained from Kanto Chemical was washed with 10% aqueous solution of sodium hydrogen sulfite, 5% aqueous solution of sodium hydroxide and saturated solution of sodium chloride, dried over sodium sulfate and then calcium hydride, and distilled under reduced pressure before use. Vinyl acetate (VAc) obtained from Kanto Chemical was distilled before use.

Benzoyl peroxide (BPO) and 2,2'-azobisisobutyronitrile (AIBN) obtained from Kanto Chemical was recrystallized from methanol before use. Ionic liquid (IL), 1-butyl-3-methylimidazolium hexafluorophosphate, was synthesized by the method of literature.²¹ Other solvents and reagents were purified by ordinary methods.

Radical polymerization of vinyl monomer initiated by BPO and AIBN in the presence of carbon black

The radical graft polymerization of vinyl monomers initiated by BPO or AIBN in the presence of carbon black was carried out in a sealed tube under vacuum. A typical example was as follows. Into a polymerization tube, 0.10 g of carbon black, 5.0 mL of vinyl monomer, 10.0 mL of solvent, 0.10 g of BPO (or AIBN), and a stirrer bar were charged. The mixture was frozen in a liquid nitrogen bath, degassed with a vacuum pump and then thawed. After this operation was repeated three times, the tube was sealed under high vacuum. The sealed tube was heated with stirring. After the graft polymerization, the products were poured into large excess of methanol to precipitate the product. The precipitate was filtered and dried *in vacuo* at 30°C. The conversion was determined by the following equation:

$$\text{Conversion (\%)} = [(A - B)/C] \times 100,$$

where *A* is weight of precipitate, *B* is weight of carbon black charged, and *C* is weight of monomer used.

Determination of percentage of grafting

To isolate ungrafted polymer from carbon black, the product was dispersed in THF and the dispersion was allowed to centrifuge. The supernatant solution containing ungrafted polymer was removed and the precipitate was dispersed in THF again. The procedures were repeated until no more polymer could be detected in the supernatant solution: the absence of ungrafted polymer in the supernatant THF solution was confirmed after the evaporation of THF. The percentage of grafting and grafting efficiency were determined by the following equations:

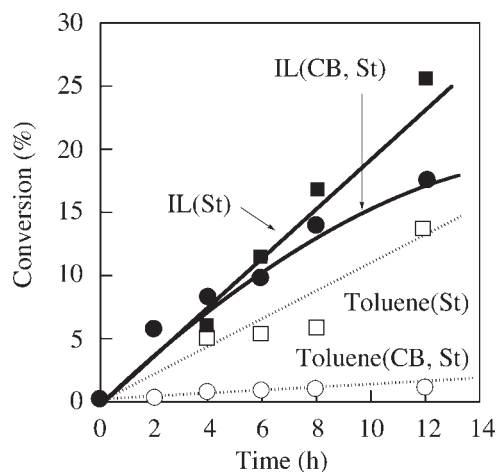


Figure 1 Polymerization of styrene initiated by BPO in the presence of carbon black. Carbon black, 0.10 g; BPO, 0.10 g; styrene, 5.0 mL; solvent, 10.0 mL; 60°C.

$$\text{Grafting (\%)} = (D/B) \times 100,$$

$$\text{Grafting efficiency} = (D/F) \times 100,$$

where D is weight of polymer grafted, B is the carbon black charged, and F is weight of total polymer formed. The weight of polymer grafted onto the surface was determined by weight loss when polymer-grafted carbon black was heated from room temperature to 500°C under nitrogen at 10°C/min by using of a thermogravimetric analyzer (TGA) (Shimadzu TGA-50).

Characterization

Fourier transform infrared (FTIR) spectra were recorded by a FTIR spectrometer (FTIR-8200A Shimadzu Manufacturing Co.) using KBr pellet.

Grafted polymer on carbon black surface was identified by thermal decomposition gas of grafted polymer by using gas chromatography-mass spectroscopy (GC-MS). The thermal decomposition GC-MS was recorded by a GCMS-QP2010 gas chromatograph mass spectrometer (Shimadzu Manufacturing Co.) equipped with a double shot pyrolyzer (Frontier Laboratories). The GC was equipped with Ultra ALLOY-5 column (30 m by 0.25 mm i.d., 0.25- μ m film thickness). Helium was used as the carrier gas. The column was programmed from 70 to 320°C at a heating rate of 20°C/min and then held at 320°C for 5 min.

RESULTS AND DISCUSSION

Radical graft polymerization of styrene initiated by BPO in the presence of carbon black

As mentioned above, we have reported that the radical polymerization of styrene initiated by BPO was

remarkably retarded in the presence of carbon black, and during the polymerization, a part of polymer formed was grafted onto the surface based on the termination (trapping) of growing polymer radical by carbon black.^{4,5} Therefore, the effect of IL on the radical polymerization in the presence of carbon was investigated.

Figure 1 shows effect of IL on the radical polymerization of styrene initiated by BPO in the presence of carbon black. It was found that when toluene was used as solvent, the polymerization was remarkably retarded. It is interesting to note that in IL, the retardation of polymerization observed in the presence of carbon black was almost disappeared in the initial stage of the polymerization.

Figure 2 shows the relationship between the reaction time and percentage of polystyrene grafting onto carbon black surface. In toluene, the grafting of polystyrene onto the carbon black surface was less than 1%. On the contrary, in IL, the percentage of grafting increased with increasing reaction time and reached 4.5%.

Figure 3 shows the relationship between conversion and grafting efficiency in the polymerization shown in Figure 1. It is interesting to note that the grafting efficiency in IL was larger than that in toluene. This indicates that the formation of ungrafted polymer was reduced in IL at the initial stage of the polymerization. But the grafting efficiency even in IL remarkably decreased with progress of the polymerization. This may be due to the fact that the trapping of growing polymer radicals on the surface are inhibited at the last stage of the polymerization because of steric hindrance of grafted polymer chains.

Figure 4 shows the decomposed gas chromatogram of (A) carbon black obtained from the poly-

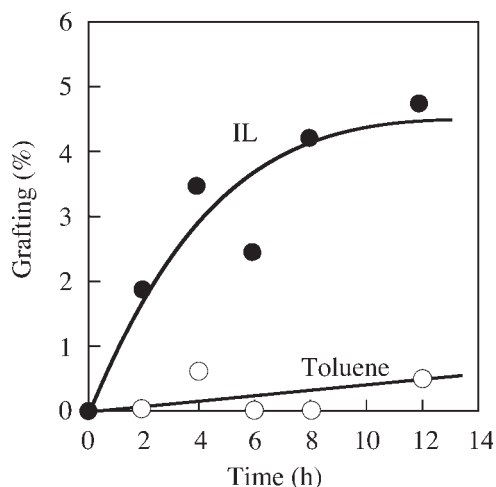


Figure 2 Relationship between polystyrene grafting onto carbon black and reaction time. Polymerization conditions are given in Figure 1.

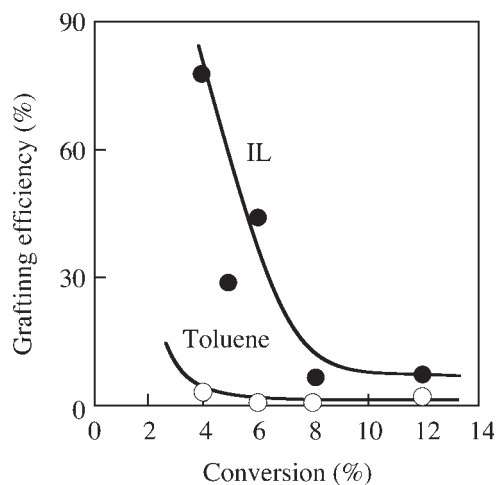


Figure 3 Relationship between grafting efficiency of polystyrene onto carbon black and conversion. Polymerization conditions are given in Figure 1.

merization of styrene in IL and (B) ungrafted polystyrene. Gas chromatogram of the decomposed gas was in agreement with that of ungrafted polystyrene. As shown in Figure 5, mass spectra of decomposed gas of polystyrene-grafted carbon black at retention time of 2.0 min were also in agreement with that of polystyrene. The results indicate the grafting of polystyrene onto carbon black surface.

It was found that FTIR spectra of polystyrene-grafted carbon black show new absorption at 700 cm^{-1} , which is characteristic of polystyrene.

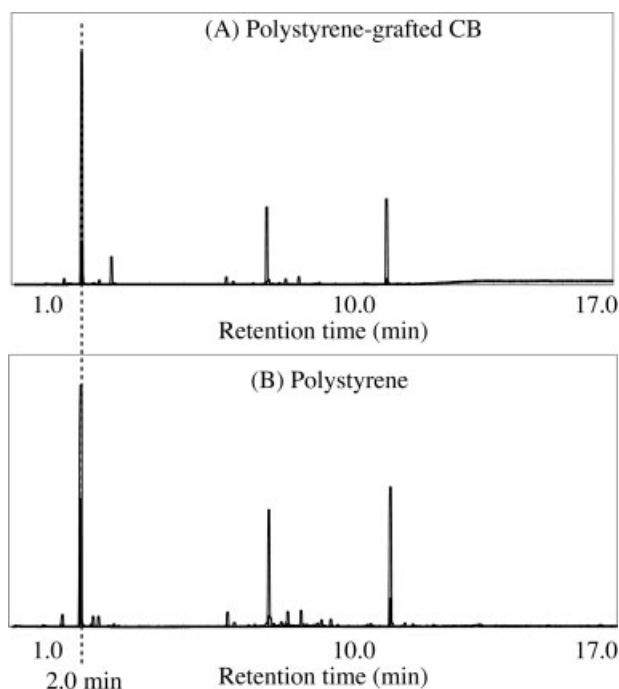


Figure 4 Thermal decomposition GC of polystyrene-grafted carbon black and polystyrene obtained from the radical polymerization of styrene in IL.

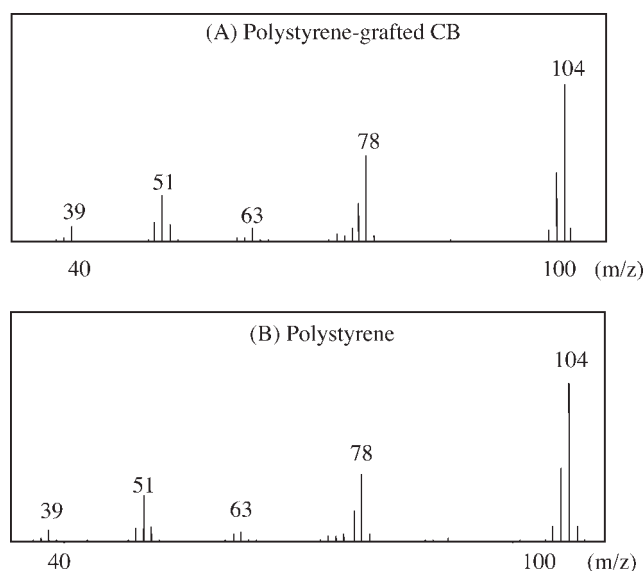


Figure 5 MS of thermal decomposition gas of polystyrene-grafted carbon black and polystyrene at retention time of 2.0 min.

Molecular weight of polystyrene

Table I shows molecular weight of polystyrene obtained from the polymerization initiated by BPO in the presence and absence of carbon black in toluene and IL. It is interesting to note that the molecular weight of polystyrene formed in IL was much larger than that in toluene. In the presence of carbon black, molecular weight of polystyrene was considerably lower than that in the absence of carbon black.

Based on the above results, it is suggested that in toluene, initiating radicals (benzoyloxy radicals) were preferentially trapped by carbon black surface and the polymerization is retarded to give lower molecular weight polymer as shown in Scheme 1. On the contrary, in IL, the growing polystyryl radicals with relatively high molecular weight were trapped by carbon black surface to give polystyrene-grafted carbon black with higher molecular weight, because of stabilization of polymer radicals in IL as also shown in Scheme 1.

TABLE I
Molecular Weight of Polystyrene Obtained from the Polymerization Initiated by BPO in the Presence of Carbon Black

Solvent	Carbon black	Conversion (%)	M_w ($\times 10^{-4}$)	M_w/M_n
Toluene	Presence	2.1	0.3	1.24
Toluene	Absence	11.1	8.9	1.19
IL	Presence	20.0	10.8	1.52
IL	Absence	39.1	42.6	3.78

Carbon black, 1.0 g; BPO, 0.1 g; styrene, 5.0 mL; solvent, 10.0 mL; 60°C ; 12 h.

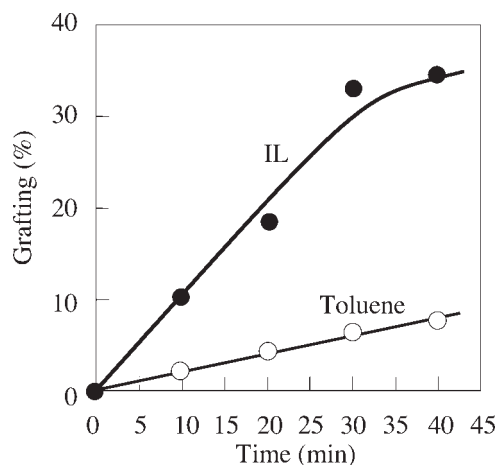


Figure 6 Relationship between polyMMA grafting onto carbon black and reaction time. Carbon black, 0.10 g; BPO, 0.10 g; MMA, 5.0 mL; solvent, 10.0 mL; 60°C.

Radical polymerization of MMA and VAc initiated by BPO in the presence of carbon black

The effects of IL on the radical polymerization of MMA and VAc in the presence of carbon black initiated by BPO were investigated. It was found that the rate of the polymerization in IL was higher than that in toluene. In addition, it is interesting to note that the inhibition and retardation of polymerization by carbon black were remarkably reduced in IL.

Figures 6 and 7 show the relationship between reaction time and percentage of grafting of polyMMA and polyVAc during the polymerization. The percentage of polyMMA grafting in IL was considerably larger than that in toluene. It is interesting to note that percentage of grafting of polyMMA was much larger than that of polystyrene and polyVAc.

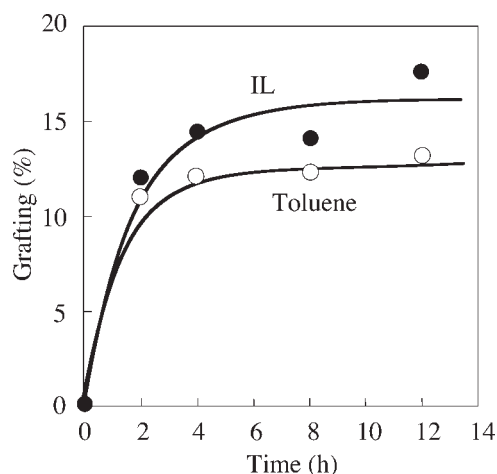


Figure 7 Relationship between poly(vinyl acetate) (polyVAc) grafting onto carbon black and reaction time. Carbon black, 0.10 g; BPO, 0.10 g; VAc, 5.0 mL; solvent, 10 mL; 60°C.

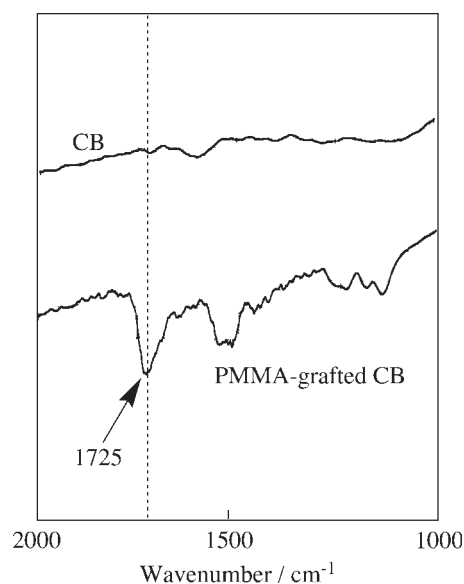


Figure 8 FTIR spectra of untreated and polyMMA-grafted carbon black.

This may be due to the difference of stability of growing polymer radicals.

The effect of IL on the grafting of polyVAc was small in comparison with that of polyMMA. This may be due to preferential chain transfer reaction in VAc polymerization.

Figures 8 shows FTIR spectra of polyMMA-grafted carbon black. The FTIR spectra show new absorption at about 1725 cm^{-1} , which is characteristic of ester groups of polyMMA. In addition, FTIR spectra of polyVAc-grafted carbon black show new absorption at about 1755 cm^{-1} , which is characteristic of ester groups of polyVAc.

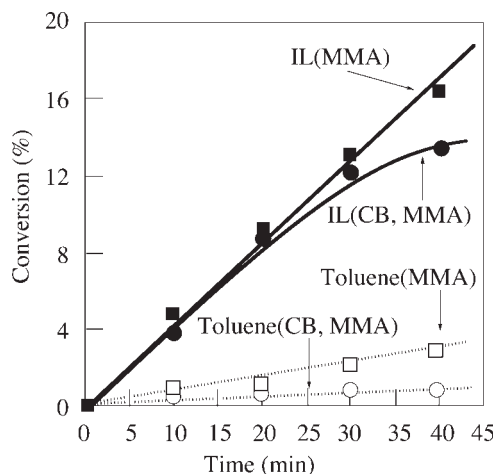


Figure 9 Polymerization of MMA initiated by AIBN in the presence of carbon black. Carbon black, 0.10 g; AIBN, 0.10 g; MMA, 5.0 mL; solvent, 10.0 mL; 60°C.

Radical polymerization of MMA and VAc initiated by AIBN in the presence of carbon black

Figure 9 shows the results of the radical polymerization of MMA in the presence of carbon black initiated by AIBN in IL and toluene. It was found that the retardation of the polymerization by carbon black was also considerably reduced in IL. In addition, it was found that the conversion increased with increasing reaction time.

Figures 10 and 11 show the relationship between reaction time and percentage of polyMMA and polyVAc grafting, respectively. It was found that the percentage of grafting increased with increasing reaction time. The percentage of grafting in IL was also considerably higher than that in toluene.

CONCLUSIONS

1. Carbon black acts as strong retarder of the radical polymerization of vinyl monomers, such as styrene, MMA, and VAc, initiated by BPO or AIBN in toluene. On the contrary, the retardation of the polymerization by carbon black was considerably reduced in IL.
2. During the polymerization, a part of polymer formed was grafted onto carbon black surface. The percentage of grafting of vinyl polymers in IL was considerably larger than that in toluene.
3. It is suggested that the growing polymer radicals with higher molecular weight were trapped by carbon black surface in IL in comparison with that in organic solvent, because of stabilization of polymer radicals.

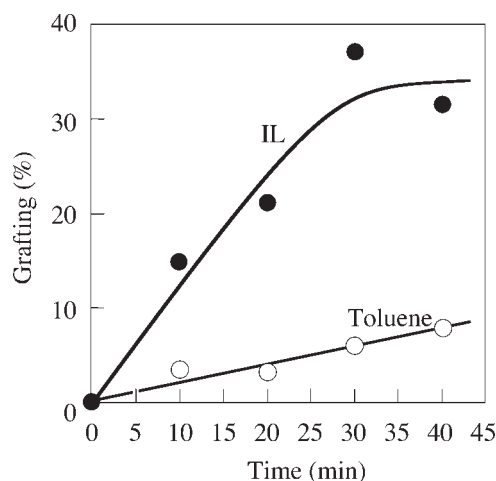


Figure 10 Relationship between polyMMA grafting onto carbon black and reaction time. Polymerization conditions are given in Figure 9.

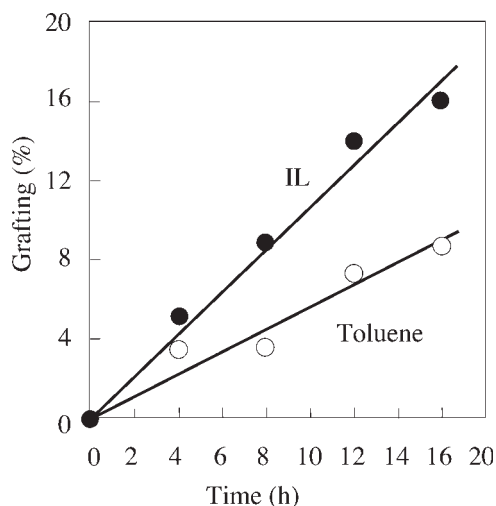


Figure 11 Relationship between polyVAc grafting onto carbon black and reaction time. Carbon black, 0.10 g; AIBN, 0.10 g; VAc, 5.0 mL; solvent, 10.0 mL; 60°C.

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