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CATIONIC GRAFT COPOLYMERIZATION OF POLYSTYRENE ONTO POLYPENTADIENE

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Keywords: Cationic polymerization, Graft copolymerization, styrene,
1,3-pentadiene

Abstract

Cationic graft copolymerizations of styrene (St) onto polypentadiene (PPD) initiated by various Lewis acids were carried out in methylene chloride. The formation of PPD-g-PSt was fully confirmed by evidences from IR and ^1H NMR. The Et_2AlCl -induced graft copolymerization gives a high St conversion and the highest grafting efficiency (GE). The effect of grafting temperature on the graft copolymerization indicates that the St conversion increases with temperature while GE shows a maximum at a temperature range around 0°C . The augmentation of PPD concentration results in increases of GE but gives rise to lower conversions. The molecular weight of the graft copolymer appears to

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decrease with the St content in graft copolymer, implying a degradation of PPD chains during the grafting process.

Introduction

The cationic polymerization of 1,3-pentadiene (PD) based C_5 petroleum fraction shows an increasing significance in the production of aliphatic petroleum resins useful in a variety of applications including adhesives, printing inks, hot-melt coatings, rubber articles and sealants [1]. This kind of resin is used rarely solely but applied mainly in combination with other components, and hence the compatibility of the resin with other substrates is quite important. As the aliphatic petroleum resin shows a relatively poor compability in many scenarios where it is used with aromatic materials such as SBR and SIS (styrene-isoprene-styrene), efforts have been made to improve compatibility of the resin with these materials by introducing aromatic groups in polymer chains of the resins. Our search for literatures indicates that, up to now, all the aromatic modifications of aliphatic petroleum resins or PD polymer (PPD) are based on copolymerzing C_5 feed or PD with aromatic monomers, e.g., styrene, α -methylstyrene, and C_9 fraction from petroleum cracking [2]. Since the sequential copolymer may exhibit more attractive properties than the corresponding radom copolymer, we decide hence to carry out the synthesis of graft copolymer PPD-g-PSt, which has never been reported in the present literature.

It is well known that the cationic graft copolymer can be synthesized by grafting *from* or grafting *onto* techniques [3]. The synthesis of PPD-g-PSt by grafting from seems difficult because it seems not convenient for PPD chains to form active species capable of initiating polymerization of St. On the other hand, double bonds in PPD chains may act as a nucleophilic site where the growing carbocation of PSt could undergo a transfer, which

permit to conduct the copolymerization of St by grafting onto technique. In fact, Minoura et al.[4] carried out the graft copolymerization of St onto chlorinated butyl rubber; Ueno et al.[5] grafted St onto natural rubber; Sigwalt et al.[6] conducted the graft copolymerization of indene onto butyl rubber, polybutadiene and ethylene-propylene-diene terpolymers; and Kennedy et al.[7] synthesized polybutadiene-g-PSt also by grafting onto method.

We report in the present work the results of our preliminary investigations on the graft copolymerization of St onto PPD with various cationic initiators in methylene chloride.

Experimental

Materials

1,3-Pentadiene from Fluka, *tert*-butyl chloride (*t*-BuCl), methylene chloride and *n*-hexane were distilled over CaH₂. Styrene was washed by 3 mol/L NaOH solution and water respectively, then dried with CaCl₂ and distilled under reduced pressure; It was distilled again over CaH₂ under reduced pressure before each usage. AlCl₃ was purified by sublimation in vacuum. Other chemicals were used as received.

Polymerization procedures

(1) *Preparation of PPD*

0.45g (3×10^{-3} mol) AlCl₃, 0.33 mL (3×10^{-3} mol) *t*-BuCl and 120 mL methylene chloride were introduced in a 500 mL three-necked-reactor in dry nitrogen atmosphere. The mixture was stirred for 15 minutes and then the polymerization was initiated by introduction of 19.8 g (0.3 mol) PD at 25°C. 2 h later the polymerization was quenched with the solvent containing a small amount of methanol. The resulting solution was filtered

to remove insoluble impurities. The filtrate was washed with water and dried by evaporation to recover PPD with a yield of 90%.

(2) *Synthesis and separation of PPD-g-PSt:*

Weight-known PPD was dissolved in methylene chloride with stirring in a three-necked-reactor in dry nitrogen atmosphere. The initiator was introduced and the reaction was achieved by adding St at last. After quenching the reaction with methylene chloride containing a small amount of methanol a given time later, the reaction solution was concentrated and *n*-hexane in large excess was added to precipitate insoluble St homopolymer. After filtration to remove homopolystyrene, the resulting solution is evaporated to recover *n*-hexane-soluble PPD-g-PSt. The difference between the weights of the recovered PPD-g-PSt and the PPD used is the weight of grafted St. The conversion of St is calculated with polymerized St including both insoluble homopolystyrene and grafted St based on used St monomer. The grafting efficiency (GE) is the ratio of the weight of grafted St (W_g) to total weight of polymerized St including grafted and homopolymerized (W_h):

$$GE(\%) = \frac{W_g}{W_g + W_h} \times 100\%$$

Measurements

IR and ^1H NMR spectra of the polymers were recorded by a Nicolet MX-1 spectrometer and by a AC-P300 spectrometer, respectively. Intrinsic viscosities of the polymers were determined with an Ubbelohde viscometer in toluene at 30°C.

Results and discussion

Table 1 shows the results of graft copolymerization of St onto PPD in methylene chloride at 0°C by various Lewis acids. Considerable differences are observed among these

Table 1. Graft copolymerizations of styrene onto polypentadiene by various cationic initiators in methylene chloride ^a

Run No	Initiator	St conversion (%)			GE (%)
		Total	Grafted St	Homopolymer	
1	AlCl ₃	~100	24.0	76.0	24
2	EtAlCl ₂	96.5	56.5	40.0	60
3	Et ₂ AlCl	90.0	66.0	24.0	73
4	TiCl ₄	12.0	0.3	11.7	2.5
5	BCl ₃	60.3	41.3	19.0	67
6	SnCl ₄	25.0	5.0	20.0	20
7	BF ₃ OEt ₂	~100	8.0	92.0	8

^a [PPD] = 2 mol/L; [St] = 2 mol/L; [Initiator] = 2×10^{-2} mol/L; Reaction temperature: 0°C; Time: 1.5 h.

initiators. We have previously shown that strong Lewis acids such as AlCl₃ and AlCl₃-based initiating systems are suitable for PD polymerization and copolymerization to give relative high conversions and molecular weights [8-11]. However, the AlCl₃-initiated graft copolymerization of St onto PPD gives a low GE in spite of a high conversion, indicating that the strong acidity of AlCl₃ gives rise to active chain transfers to monomer resulting in the formation of homopolystyrene. Consequently, the decrease in initiator acidity leads to an increase of GE as well as a slight drop in conversion. With EtAlCl₂ and Et₂AlCl, GE values of 60% and 73% were obtained, respectively. The graft copolymerizations induced by other initiators fail to exhibit appreciable results. The grafting by BCl₃ gives a relatively high GE with a conversion of 60%. The BF₃OEt₂-induced reaction results in a complete conversion but with a rather low GE.

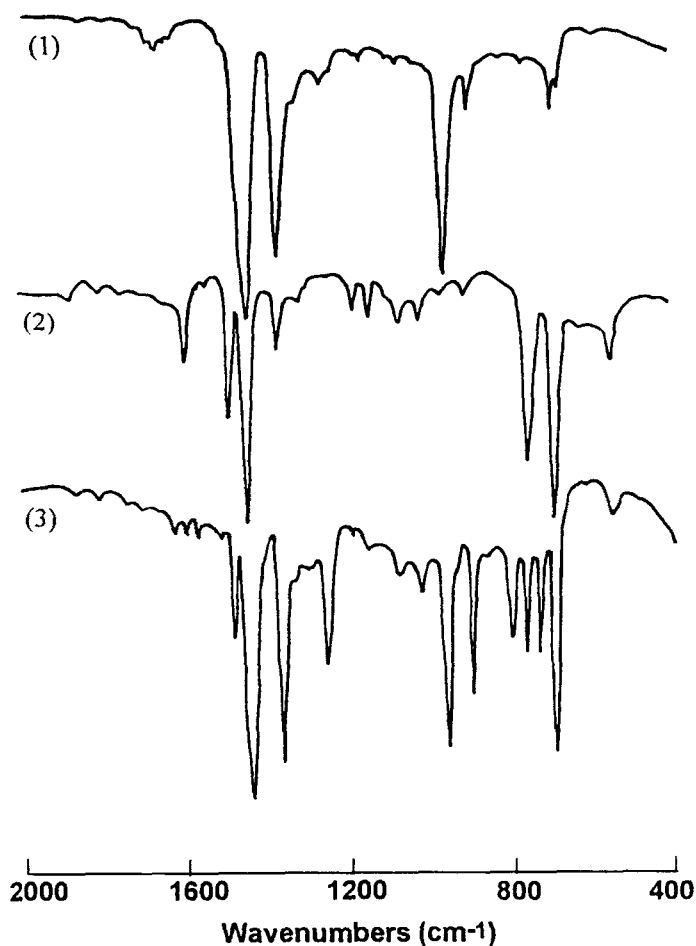


Figure 1. IR spectra of the polymers. (1) PPD; (2) homopolystyrene obtained by Run 3 in Table 1; (3) graft copolymer obtained by Run 3 in Table 1. Reaction conditions are given by Table 1.

The formation of PPD-*g*-PSt could be fully confirmed by evidences from IR and ^1H NMR. Figure 1 shows IR spectra of *n*-hexane-insoluble part (No 2) and *n*-hexane-soluble part (No 3) obtained by Run 3, compared with the spectrum of PPD (No 1). The spectrum 2 is a typical spectrum of polystyrene, which evidences that the *n*-hexane-insoluble part is St homopolymer. On the other hand, the spectrum 3 shows all the main sepecific peaks

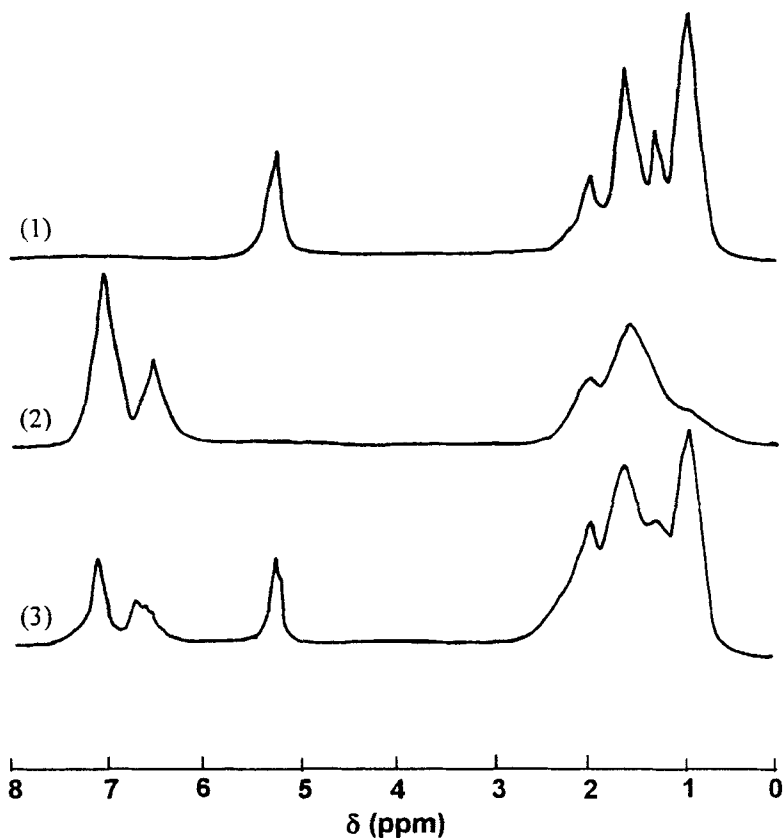
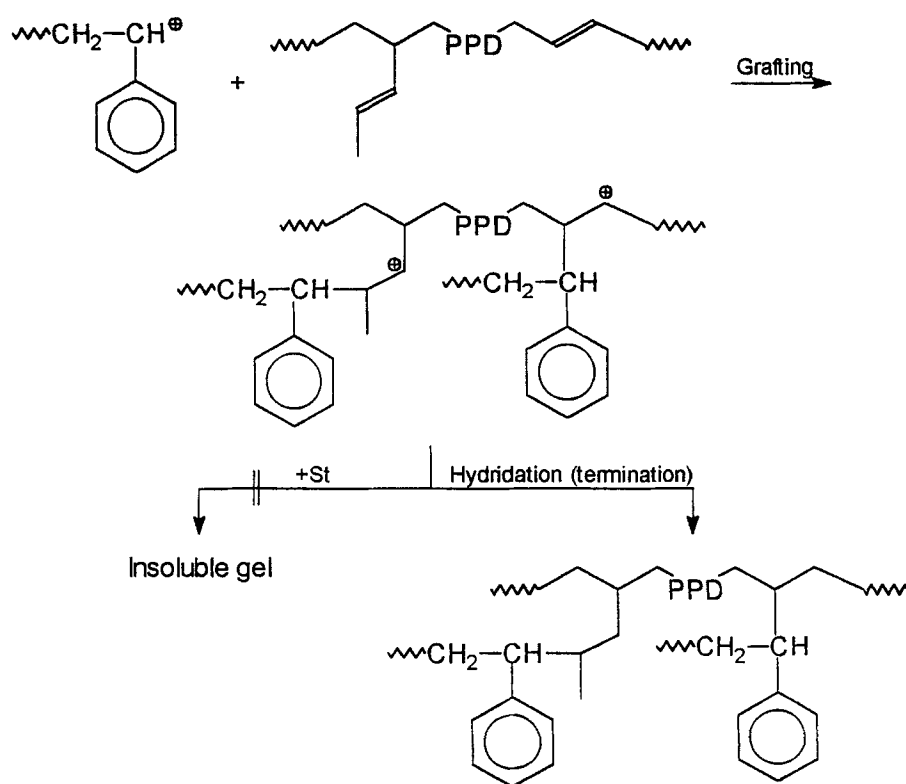


Figure 2. ¹H NMR spectra of the polymers. (1) PPD; (2) homopolystyrene obtained by Run 3 in Table 1; (3) graft copolymer obtained by Run 3 in Table 1. Reaction conditions are given by Table 1.

given by spectra 1 and 2, indicating that the *n*-hexane-soluble polymer is PPD-St copolymer. Besides, the spectrum 3 shows also several bands at 1270cm⁻¹, 910cm⁻¹, 820cm⁻¹ and 750cm⁻¹ which are not given by PPD and PSt. These new absorptions probably arise from the covalent linkage between PPD chains and PSt branches.

¹H NMR spectra of the polymers are shown in Figure 2. Similarly, the signals arising from PPD (No 1) and PSt (No 2) are all present in the spectrum of the graft copolymer (No 3), indicating that amounts of St were grafted onto PPD backbone.

According to P. Sigwalt et al. [6], the grafting onto unsaturated backbones involves transfers of branch growing carbocations to double bonds of unsaturated chains and hence the newly formed carbocation in backbone chains is potentially capable of initiating a new propagation to generate insoluble gel (crosslinked polymers). Kennedy et al. [7] also pointed out that the formed carbocation can undergo two reaction routes, i.e., reinitiation (to give crosslinking) or termination by hydridation. The experimental fact that our graft copolymerization does not produce any gel suggests that the newly generated carbocations in PPD chains pursue mainly a termination by rapid hydridation instead of undergoing a new initiation. Therefore, the present graft copolymerization of styrene onto polypentadiene can be schematically illustrated in the following reactions:



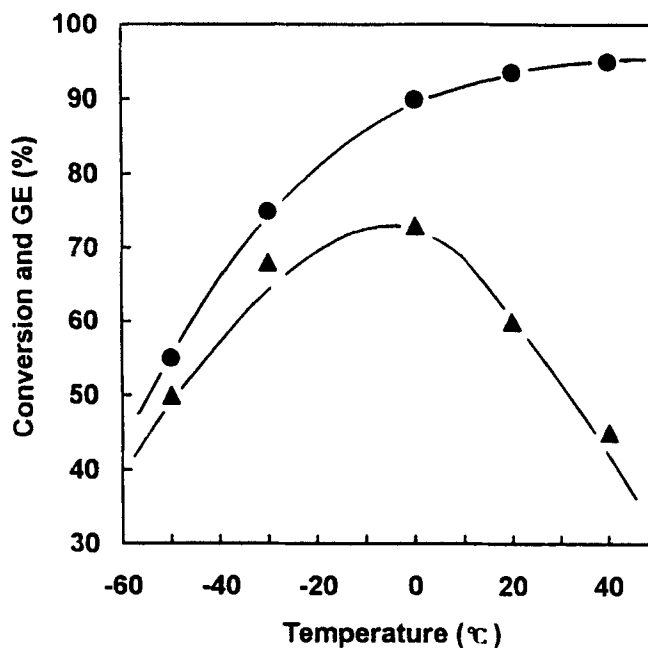


Figure 3. Effect of temperature on St conversion (●) and GE (▲) for the graft copolymerization initiated by Et_2AlCl . See Table 1 for reaction conditions.

Figure 3 shows the effect of temperature on the graft copolymerization initiated by Et_2AlCl . It is observed that the St conversion increases with the reaction temperature. On the other hand, the grafting efficiency appears a maximum with temperature variation, and the graftings at both high or low temperatures give small GE values. Therefore, only the graft copolymerization carried out in a temperature range around 0°C gives appreciable conversion and GE. In fact, the grafting efficiency is determined by both transfer to unsaturated segments of PPD (grafting) and chain-breaking processes resulting in homopolystyrenes which embrace transfer to monomer and termination by hydridation. Higher temperatures give rise to more active transfer to monomer and hence low GE values are obtained [6]. On the other hand, lower temperatures probably reduce the

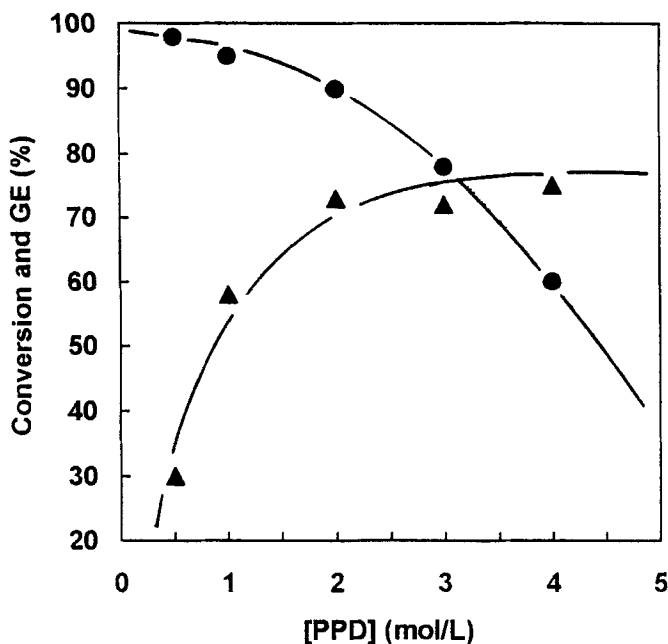


Figure 4. Effect of concentration of PPD on St conversion (●) and GE (▲) for the graft copolymerization initiated by Et_2AlCl . See Table 1 for reaction conditions.

activity of St growing species and hence the termination becomes dominant over the transfer to unsaturated units of PPD.

Figure 4 gives the effect of the concentration of the backbone polymer on the graft copolymerization. The grafting at low PPD concentrations gives rise to high St conversion but low GE due to small double bond content in PPD chains where grafting takes place. The augmentation of PPD concentration results in higher GE values but relatively low St conversions. In another word, the presence of PPD in high concentration substantially inhibit the polymerization of styrene under the present reaction conditions.

Figure 5 summarizes the dependence of the intrinsic viscosity of the graft copolymer on the St proportion in the graft copolymer. It is found that the intrinsic viscosity

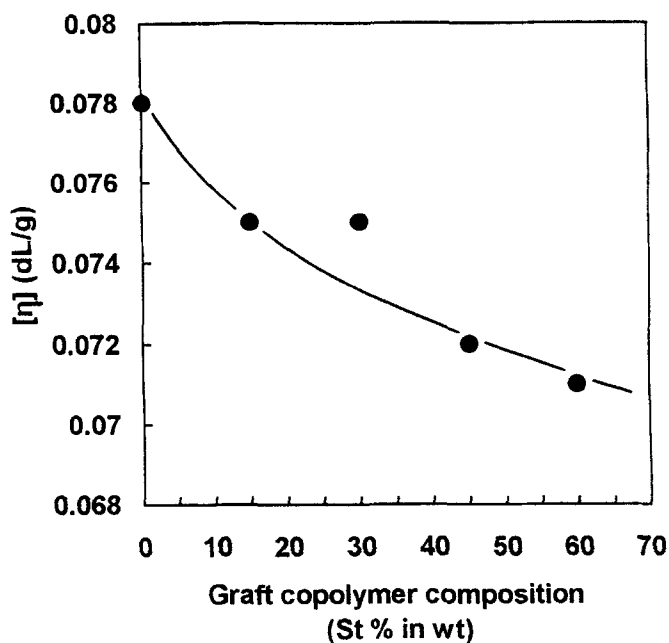


Figure 5. Dependence of the intrinsic viscosity of PPD-g-PSt on the graft copolymer composition.

decreases with the St content in the copolymer, which demonstrates that the molecular weight of the PPD was reduced by attaching St branches on it. This result is probably due to a slight degradation of PPD chains during the grafting process, that is, the chain scission reaction take place during the grafting conditions. In fact, this kind of degradation was also observed by Sigwalt in the grafting of indene onto unsaturated backbones [6]. It must be said that the intrinsic viscosity is influenced not only by the molecular weight but also by the polymer shape. Investigations along this line is worthy.

Conclusions

1) Poly(1,3-pentadiene)-g-polystyrene (PPD-g-PSt) was synthesized by cationic *grafting onto* method and the formation of the graft copolymer was fully confirmed by evidences from IR and ^1H NMR.

2) The syntheses of PPD-g-PSt in methylene chloride at 0°C were initiated by various Lewis acids and the Et₂AlCl-induced graft copolymerization gives the highest grafting efficiency (GE).

3) The St conversion of the graft copolymerization initiated by Et₂AlCl increases with the grafting temperature while GE shows a maximum at the range around 0°C.

4) The augmentation of the backbone polymer (PPD) gives rise to increases in St conversion but decreases in GE.

5) The intrinsic viscosity of the graft copolymer decreases gradually with the grafted St content due to a slight degradation of PPD chains.

Acknowledgement

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