Iranian Polymer Journal
17 (5), 2008, 379-388

Available online at: http://journal.ippi.ac.ir

NMR Study of Grafting Polystyrene on Low Molecular Weight Polybutadiene in Thermal Polymerization

Farshid Ziaee*, Hamid Salehi Mobarakeh*, Mehdi Nekoomanesh, and Hassan Arabi

Iran Polymer and Petrochemical Institute, P. O. Box 14965/115, Tehran, Iran

Received 12 February 2008; accepted 13 May 2008

A B S T R A C T

In this study styrene was thermally polymerized by solution method in the presence of low molecular weight polybutadienes (PBDs) at 100, 175, 250ºC. Two types of PBD with various contents of 1,2-vinyl and *cis*/*trans* isomers were employed. Using PBDs of low molecular weight allowed the study of grafting mechanisms by soluble grafted products obtained for liquid nuclear magnetic resonance (NMR) characterization. The effect of polymerization temperature and the type of polybutadiene on grafting degree were investigated. It is shown that grafting of polystyrene (PS) on PBD increases with increasing 1,2-vinyl content and temperature of polymerization. Accordingly, PBD with high 1,2-vinyl content and polymerization at 250ºC gave the highest grafting efficiency. However, grafting was identical for *cis* and *trans* isomers in 1,4-PBD. Liquid $^{13}C\{^{1}H\}$NMR spectroscopy using distortion enhancement by polarization transfer (DEPT) techniques were performed and a mechanism of grafting was proposed based on addition reaction with reducing the unsaturated olefinic double bonds without formation of any quaternary olefinic or aliphatic carbons. With quantitative analysis of triad sequences of 1,2-PBD methylene carbon before and after grafting, it was shown that polystyrene chains mainly graft on syndiotactic sequences of 1,2 PBD.

Key Words:

grafting;
styrene;
polybutadiene;
thermal polymerization;
NMR.

INTRODUCTION

Grafting of polystyrene on polybutadiene during styrene polymerization in high impact polystyrene (HIPS) process has been widely studied [1-15]. In industrial operations, methods of radical polymerization with or without initiator are used. In the literature more references can be found on application of initiator compared with thermal polymerization process of HIPS production. In polymerization with initiator, the type of initiator has a great impact on the polymerization process. For instance benzoyloxy radicals which are formed during decomposition of benzoyl peroxide initiator are bonded to PBD chains

(*) To whom correspondence to be addressed.
E-mail: f.ziaee@ippi.ac.ir
h.salehi@ippi.ac.ir

by opening double bonds in PBD chains, while using azobisisobutyronitrile (AIBN) would decrease grafting reactions [16-20]. In fact AIBN does not attack PBD chains and only polystyryl macroradicals react with PBD chains leading to reduction of the graft content [17-21]. Similarly, peroxide initiated grafting gives higher grafting efficiency than thermal initiation [16-20]. In free radical polymerization, reaction temperature has no effect on PBD rearrangement and cross-linking while in thermal polymerization at temperatures above 200ºC it may thermally induce rearrangement and cross-linking in PBD chains [22-23].

Therefore, part of grafting and gelation in thermal polymerization of styrene in the presence of PBD is due to the linkage formation among polybutadiene chains themselves. Both in the literature and industrial plants, use of high molecular weight PBDs is reported in which some insoluble gels are formed in the final stages of HIPS productions [24-28]. In this study, in order to avoid gel formation and cross-linking, the polybutadienes of low molecular weights were used which allowed appropriate separation space and solubilization of grafted PBD in order to perform liquid nuclear magnetic resonance (NMR) investigations.

Concerning grafting mechanisms several reports can be retrieved from the literature including different chemical grafting reactions. Among them the addition reaction accompanied with some double bond disappearance [29-30] and grafting without altering unsaturation, based on hydrogen abstraction, can be encountered. In the last decades, NMR spectroscopy has shown its capability in microstructural investigations of polymers [31-34]. PBD and polystyrene (PS) have been analyzed with this technique which is further advanced through various experiments such as DEPT [35-36]. However, detailed NMR study on thermal polymerization of styrene in the presence of low molecular PBD has not been reported before. In this study the effective parameters and mechanisms of grafting for the polymerization are investigated by NMR spectroscopy.

EXPERIMENTAL

Materials

Styrene monomer was obtained from Merck Chemical Co. Inc. To remove the inhibitor it was washed three times with a 5% sodium hydroxide solution followed by three times distilled water and then dried over calcium chloride. Freshly distilled monomer under vacuum was used. 1,2-PBD(46, 686-7) and 1,4-PBD(43, 477-9) were purchased from Aldrich and used as received. Their molecular weight and isomer contents were determined with gel permeation chromatography (GPC) and ^{1}H NMR [37] analysis. Table 1 represents the properties of PBDs. Solvents (benzene, chloroform, ethyl acetate from Merck, and n-heptane and methanol of technical grades) were used without further purification.

Polymerization

Thermal polymerization of styrene was conducted in stainless steel ampoules sealed under vacuum at 10^{-1} mmHg. The ampoules were 15 cm in length with an inlet diameter of 8 mm and wall thickness of 2 mm. The ampoules were degassed by several vacuum freeze-thaw cycles and polymerizations were carried out in oil bath. Thermal solution polymerization was conducted at 100, 175 and 250ºC and maintained constant within ±0.1°C of the desired temperature. Termination of the polymerizations was enforced by quenching the ampoules in liquid nitrogen. The typical recipes studied were as follows: repeating unit of butadiene 5M, styrene 1M and benzene 5M. After

Table 1. Characterization of polybutadienes.

Type of polybutadiene	$\overline{M}_n$*	$\overline{M}_w$*	Cis (%)**	Trans (%)**	1,2-Vinyl (%)**
1,2-PBD	3700	5000	4	11	85
1,4-PBD	2700	7500	75	24	1

(*) Measured by GPC and (**) ^{1}H NMR in this study.

reaction the polymers were added to cold n-heptane and precipitated polystyrene homopolymer was separated after 24 h storage in cold place (about 5ºC) or half hour of centrifuging at 7500 rpm, and then dried. Dried samples were dissolved in chloroform and precipitated in 25-fold excess of chilled methanol. The filtrate was washed and dried at 40°C under vacuum to constant weight. Solution of n-heptane which contained polybutadiene and polystyrene grafted to polybutadiene (PS-*g*-PBD) was evaporated under vacuum and the residue was dried. It was then dissolved in chloroform and fractional precipitation was performed by dropwise addition of methanol. Finally, the two phases were decanted and each part was precipitated in excess methanol, filtered and dried at 40°C under vacuum to constant weight. Thus, free polybutadiene, homopolystyrene and graft copolymer were successively separated, weighed and confirmed by ^{1}H NMR. As controls, homopolystyrene was prepared by solution polymerization in benzene with the same recipe and PBD was heated in the absence of styrene monomer.

Characterization

The liquid NMR spectra were recorded on a Bruker Avance 400 MHz. Sample concentration was about %20 (w/v) for ^{13}C NMR and %5 (w/v) for ^{1}H NMR using a 5 mm NMR tube at room temperature. ^{1}H NMR spectra were acquired using 32K data points, spectral width 16 ppm, acquisition time 1.97s, relaxation delay 60s, pulse width 30º, 4 scans. ^{13}C NMR spectra were acquired using 64K data points, spectral width 220 ppm, acquisition time 1.37s, relaxation delay 10s, pulse width 90º, 10000 scans and the Nuclear Overhauser Effect was suppressed by gating the decoupler sequence.

The J-modulation time for the DEPT sequence was set at 3.57ms after finding high power pulse for 90 and 180 degrees. DEPT was acquired using 64K data points, 10000 scan, dummy scan 8, acquisition time 1.37s and relaxation delay 10s. Molecular weights and polydispersity of the polystyrenes were determined by gel permeation chromatography (GPC) consisting of an Agilent 1100, differential refractometer detector and PLgel columns 10 µm series (500 Aº, 10^3 Aº, 10^4 Aº) and (10^3 Aº, 10^4 Aº, 105 Aº) with THF as the eluent at a flow rate of 1mL/min at 30ºC.

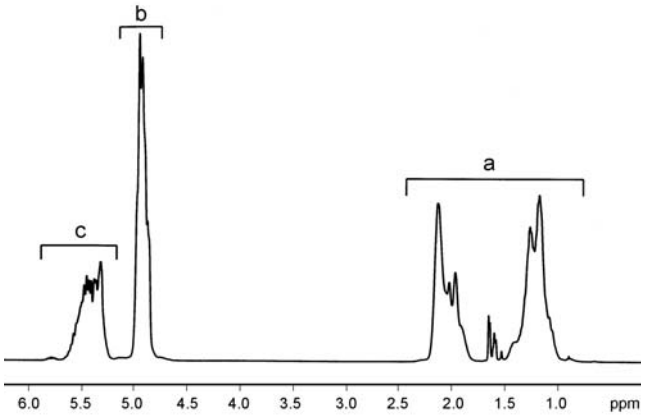


Figure 1. ^{1}H NMR spectrum of 1,2 polybutadiene before grafting in $CDCl_3$ at room temperature.

RESULTS AND DISCUSSION

Grafting by ^{1}H NMR investigation

Figures 1 and 2 show ^{1}H NMR spectra of 1,2-polybutadiene and 1,4-polybutadiene, respectively. As it is seen from Figures 1 and 2, peak areas corresponding to olefinic and aliphatic protons can be measured separately. In both spectra of PBD, aliphatic protons appear at 0.7-3.0 ppm (assigned a) and olefinic PBD protons appear at 4.6-5.9 ppm (assigned b and c). The ratio of olefinic protons peak area to the sum of both proton types gives mole percent of olefinic protons using eqn (1).

Percent of olefinic proton for polybutadiene =

$$\frac{b+c}{a+b+c}\times 100 \qquad (1)$$

On the other hand in olefinic protons region, methylene protons of 1,2-vinyl isomer at 4.6-5.1 ppm (assigned b) and olefinic methine protons of all

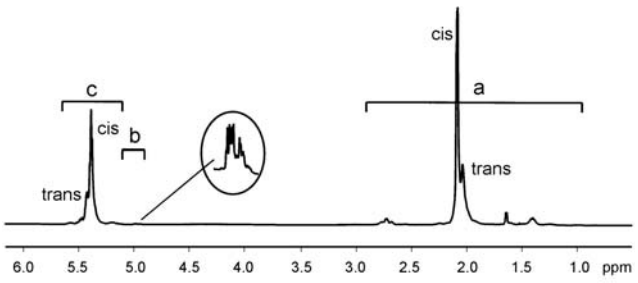


Figure 2. ^{1}H NMR spectrum of 1,4-polybutadiene before grafting in $CDCl_3$ at room temperature.

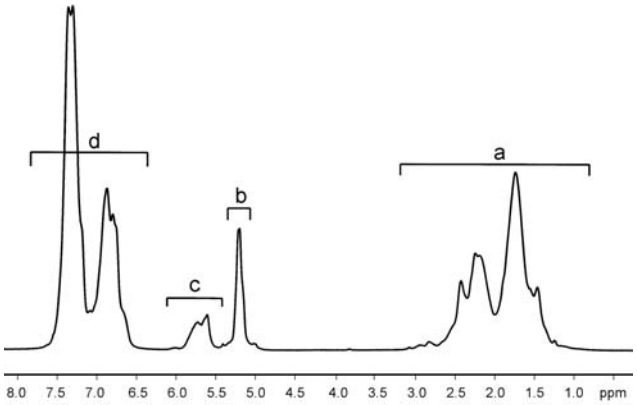


Figure 3. ^{1}H NMR spectrum of PS-*g*-1,2-PBD in $CDCl_3$ at room temperature.

1,2-vinyl, *cis* and *trans* isomers at 5.2-5.9 ppm (assigned c) are observed. Consequently by measuring the related peak areas using eqn (2), 1,2-vinyl content can be calculated:

$$\text{Weight percent of 1,2-vinyl} = \frac{b}{b+(c-b/2)}\times 100 \quad (2)$$

Figures 3 and 4 show polystyrene grafted on PBD (PS-*g*-1,2 PBD) and (PS-*g*-1,4 PBD) which are prepared and purified at final conversion and 250ºC, respectively. As it is observed from Figures 3 and 4, in addition to PS and PBD aliphatic protons which appear at 0.7-3.2 ppm (assigned a) and PBD olefinic protons at 4.6-5.9 ppm (assigned b and c), protons of PS phenyl appear at 6.4-7.8 ppm (assigned d). This is true for $CDCl_3$ which appears at 7.2 ppm and overlaps with phenyl protons. In fact, with respect to the concentration of polymers in the prepared NMR samples, the concentration of $CDCl_3$ with 99.9%D is negligible and the corresponding peak would overlap as well. Using these peak nomenclatures and related areas in Figures 3 and 4 with respect to repeating molar mass units the extent of PBD in each sample

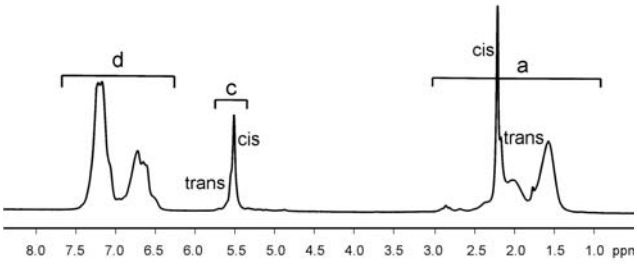


Figure 4. ^{1}H NMR spectrum of PS-*g*-1,4PBD in $CDCl_3$ at room temperature.

can be calculated through eqn (3).

Weight percent of polybutadiene =

$$\frac{9(a-(3d/5)+c+b)}{9(a-(3d/5)+c+b)+(104d/5)}\times 100 \quad (3)$$

Moreover, by using eqn (4), changes in the quantity of olefinic protons of PBD can be calculated and the results are presented in Table 2.

Percent of olefinic proton for polybutadiene in PS-g-PBD =

$$\frac{c+b}{a-(3d/5)+c+b}\times 100 \quad (4)$$

According to the obtained data reported in Table 2, the double bond contents decrease during grafting reaction. This means that double bonds in PBD chains act as monomer and are involved in the reaction though with a very low copolymerization rate. In order to verify the validity of eqns (3) and (4) in PS grafting on PBD, the homopolymerization of styrene and PBD heating under the same conditions were performed separately and the products were regarded as references and mixed at selected compositions. ^{1}H NMR spectra of these samples were recorded and eqns (3) and (4) were again applied to the NMR

Table 2. Characterization of 1,2 and 1,4-polybutadiene before and after grafting.

Type of polybutadiene	Before grafting		After grafting*	
	Olefinic proton (%)	1,2-vinyl (%)	Oefinic proton (%)	1,2-vinyl (%)
1,2-PBD	46.68	85.2	44.34	82.2
1,4-PBD	32.32	1.0	31.10	-

(*) Analysis of sample at 250ºC and full conversion.

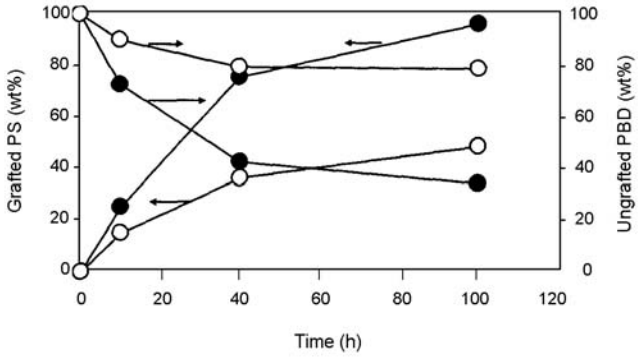


Figure 5. Grafted polystyrene and ungrafted polybutadiene versus time at 100ºC (● 1,2-PBD, ○ 1,4-PBD).

results and it was shown that the equations for the determination of olefinic proton content and PBD weight content are valid. As a result, the addition reaction according to the Fischer [29, 38] mechanism in thermal polymerization of styrene in the presence of PBD is endorsed. Furthermore, the ratio of *cis/trans* olefinic or aliphatic protons in 1,4-PBD shown in Figures 2 and 4, remains almost constant during grafting which indicates similar tendency of grafting on *cis* and *trans* isomers. It is worth mentioning that at high temperature of 250ºC there is some *cis-trans* isomerization with increasing rate of *cis* to *trans* conversion [22-23].

Study of Effective Parameters on Grafting

Generally, in thermal polymerization of styrene in the presence of polybutadiene, effective parameters on grafting include 1,2-vinyl content of PBD and polymerization temperature. In free radical polymerization by initiator, type and concentration of initiator are

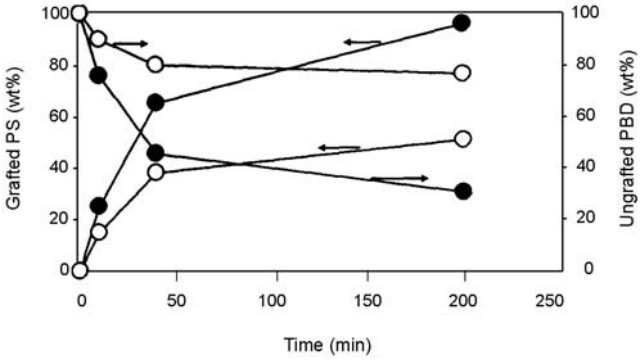


Figure 6. Grafted polystyrene and ungrafted polybutadiene versus time at 175ºC (● 1,2-PBD, ○ 1,4-PBD).

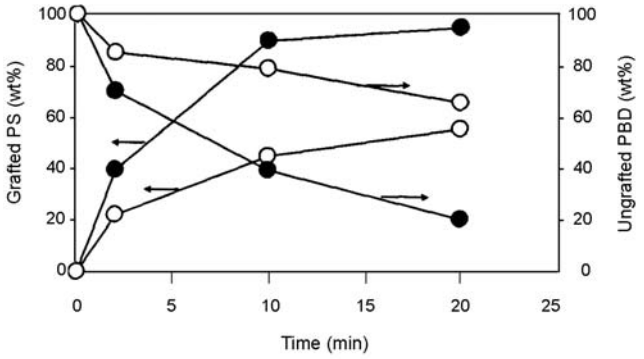


Figure 7. Grafted polystyrene and ungrafted polybutadiene versus time at 250ºC (● 1,2-PBD, ○ 1,4-PBD).

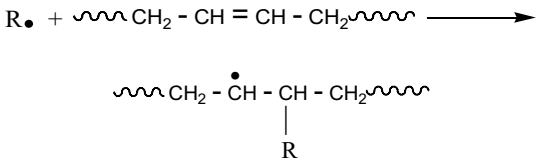
essential parameters on polystyrene grafting [38]. In industrial processes, thermal polymerization proceeds from low conversion at 70-100ºC and continues up to 240-260ºC depending on the desired properties at which final conversion is achieved. Comparatively, in this study grafting reactions were carried out at 100, 175 and 250ºC. Using high molecular weight PBD and phase conversion process, cross-linking reactions were induced which led to gel formation [24, 35]. On the other hand, low molecular weight PBD and simultaneous use of solvent during polymerization reduced gel content to a minimum level so that all products including PBD, ungrafted polystyrene and grafted PBD with polystyrene remained soluble allowing investigations to be made through liquid NMR spectroscopy [36].

Based on raw material ratios the extents of grafted PS and ungrafted PBD at different time intervals and temperatures are calculated and the results are shown in Figures 5-7. Since there is no precipitation of PS homopolymer in n-heptane after reaction with 1,2-PBD at different temperatures, the curves of grafted PS in Figures 5-7, are indications of PS conversion. As it is observed from Figures 5-7, grafting of PS on PBD increases with increasing 1,2-vinyl content, while reaction time to reach the maximum conversion decreases from 100 h to 20 min by increasing temperature. By comparing Figures 5-7, it is clearly shown that by increasing temperature the rate of grafting increases abruptly while the extent of ungrafted PBD or grafted PS change moderately. PBD with 85 percent of 1,2-vinyl isomer exhibits complete grafting of PS on PBD in a selected formulation. As it is evident,

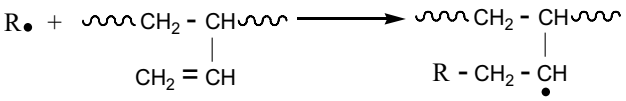
there is no precipitation on adding polymerization solution to n-heptane. The stopping time of each experimental batch was based on Husain and Hamielec time-conversion plots [39].

Investigation of Grafting Mechanism by ^{13}C NMR

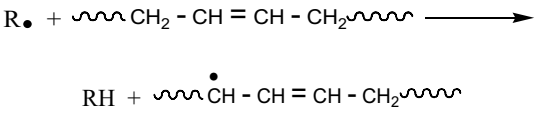
In order to compare the experimental results with proposed mechanisms in the literature at first the existing mechanisms are reviewed. In Fischer [29, 38] mechanisms, grafting is suggested through addition on 1,4 and 1,2 units and hydrogen abstraction which are as follows:



Scheme I. Addition (to 1,4 units)

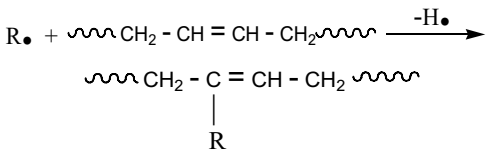


Scheme II. Addition (to 1,2 units)

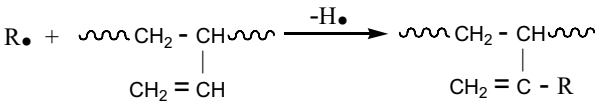


Scheme III. Hydrogen abstraction

In Fischer mechanism, the addition reactions are accompanied with unsaturation loss in PBD chains while in hydrogen abstraction a decrease in methylene carbon content takes place as well as a simultaneous increase of methine carbon content. In Lin and Liu [36] mechanism, the proposed reactions are as follows:

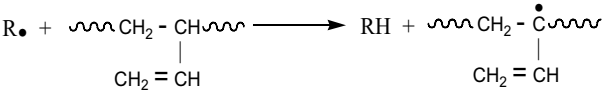


Scheme IV. Hydrogen abstraction (to 1,4 units)



Scheme V. Hydrogen abstraction (to 1,2 units)

In this mechanism, hydrogen abstraction reactions are considered ineffective on the unsaturation sites. It is proposed that methine carbon content decreases in favour of quaternary olefinic carbon formation. In Brydon [40-41] mechanism, different form of hydrogen abstraction is suggested as follows:



Scheme VI. Hydrogen abstraction

in which allylic hydrogen is abstracted from PBD chain leading to formation of quaternary aliphatic carbons.

In order to study grafting mechanism by NMR, optimum conditions are required in which the highest number of short PS chains grafted on PBD can be achieved. In this way characterization of the grafted carbons can be performed by ^{13}C NMR.

Consequently, polystyrene was prepared in the absence of PBD through bulk and solution polymerization of styrene and PS molecular weight are shown

Table 3. Characterization of homopolymerization of styrene.

Type of polymerization	Temperature (ºC)	$\overline{M_n}$	PDI	No. repeating units
Bulk	250	6500	2.4	60-65
Solution	250	3700	3.5	32-37
Bulk	100	500000	2.2	4800-4900
Solution	100	300000	2.8	2800-2900

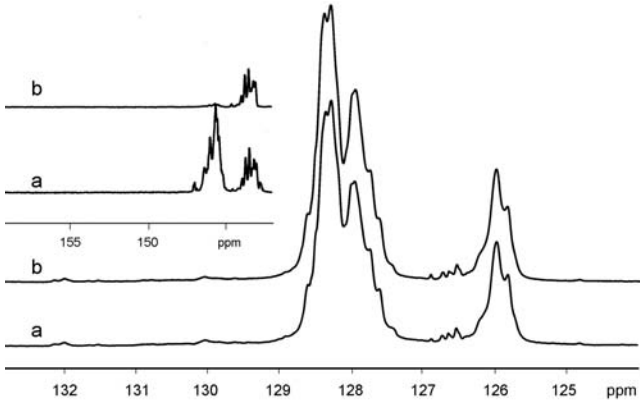


Figure 8. ^{13}C NMR (a) and DEPT45 (b) spectra of PS-*g*-1,2 PBD in $CDCl_3$ at room temperature.

in Table 3.

As it is evident in Table 3, with increasing temperature $\overline{M}_n$ decreases showing lower repeating units. Furthermore, using benzene as solvent in addition to separate PBD chains and inhibition of phase inversion act as chain transfer agent which then reduces the molecular weight of polystyrene. As a result, to study the grafting, polymerization condition was set at 250ºC, using benzene as solvent. After performing reactions and separation of PS-*g*-1,2 PBD, ^{13}C NMR and DEPT45 were obtained which are shown as a and b, respectively in Figure 8. In DEPT135, DEPT90 and DEPT45 experiments quaternary carbons are eliminated. Since, methylene and methine carbons overlap thus for characterization of the quaternary carbon atoms one can use DEPT45 technique. Lin and Liu [36], based on their NMR study, reported the presence of quaternary carbons according to Schemes IV and V. This was done using DEPT experiment in which the

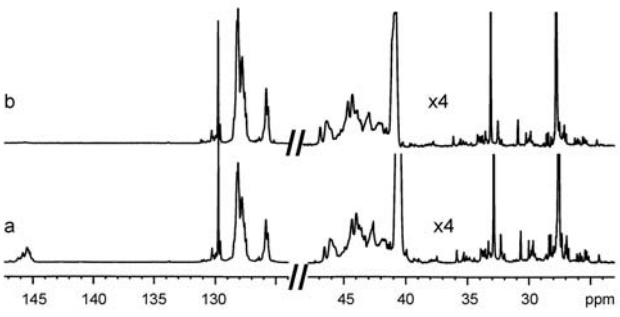


Figure 9. ^{13}C NMR (a) and DEPT45 (b) spectra of PS-*g*-1,4 PBD in $CDCl_3$ at room temperature.

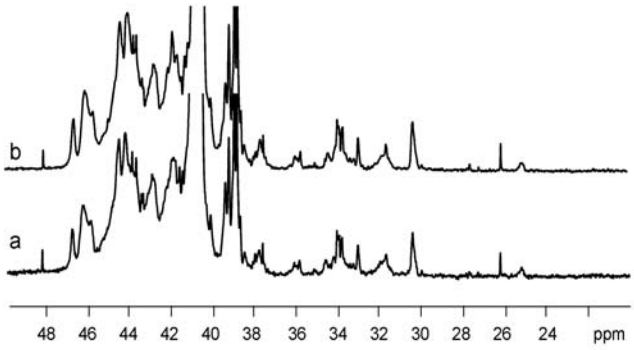


Figure 10. ^{13}C NMR (a) and DEPT45 (b) spectra of PS-*g*-1,2 PBD in $CDCl_3$ at room temperature.

quaternary olefinic carbons were characterized at 126.0 ppm and 128.4 ppm. As it is seen in Figure 8, there is no diminution in peak area viewed by DEPT compared to ^{13}C NMR. This experiment was performed for PS-*g*-1,4 PBD and similar results were obtained. Moreover, peak at 145.0-147.0 ppm in Figure 8 corresponds to quaternary carbon of phenyl which is eliminated in DEPT experiment. This carbon is present in PS spectrum and it is not related to PS-*g*-1,2 PBD.

Furthermore, using NMR software the position of olefinic quaternary carbons can be calculated. Quaternary olefinic carbon which is formed during grafting of PS on PBD with 1,2-vinyl units as shown in Scheme V is predicted to have appeared at 156 ppm which is not observed in Figure 8. Moreover, if grafting happens on *cis* and *trans* isomers as shown in Scheme IV, quaternary olefinic carbons should be seen at about 141 ppm. Figure 9 shows ^{13}C NMR and DEPT45 spectra of PS-*g*-1,4 PBD. As it is seen in Figure 9, in this region no quaternary carbons are seen which indicate no hydrogen abstraction occurred on olefinic carbon and consequently the quaternary olefinic carbons are not produced in thermal polymerization of styrene in the presence of PBD. On the other hand, according to hydrogen abstraction mechanism proposed by Brydon as shown in Scheme VI the formation of aliphatic quaternary carbon may be traced.

Brydon showed that allylic hydrogen of 1,2-PBD is abstracted by radicals from initiator decomposition. According to Scheme VI and based on software calculations, the quaternary aliphatic carbon will appear

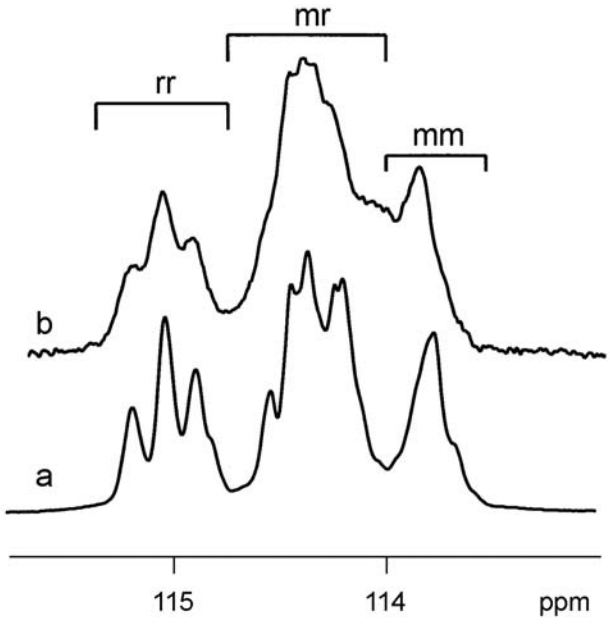
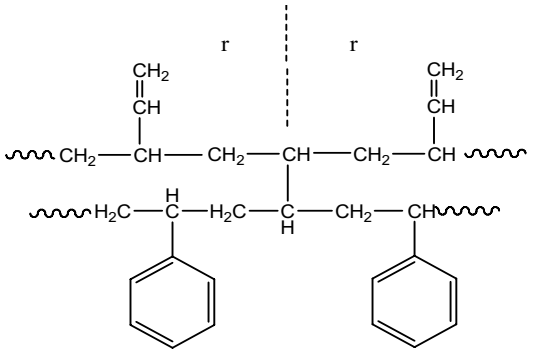


Figure 11. ^{13}C NMR spectrum of olefinic methylene carbon, 1,2 PBD (a) and PS-*g*-1,2 PBD (b) in $CDCl_3$ at room temperature.

at 27 ppm. Figure 10 shows ^{13}C NMR spectrum and DEPT45 experiment of PS-*g*-1,2 PBD. As it is seen from Figure 10 there is no quaternary carbon formation which means hydrogen abstraction has not occurred on allylic structures. In the end, addition mechanisms on 1,2-vinyl are specially preferred and in order to obtain most probable mechanism in this study, triad sequences of pendant groups have been analyzed. Figure 11 shows ^{13}C NMR spectra of olefinic methylene carbon for 1,2-PBD before and after grafting.

Methylene carbons of 1,2-PBD appear at 113.5-115.5 ppm which is separated from other absorption bands. These carbons and their triad sequences [42-44] are shown in Figure 11a.

By normalizing peak area each triad extent can be calculated quantitavely. In the Figure 11, r and m stand for *racemic* and *meso*, respectively and rr, mr and mm show the extent of syndiotacticity, atacticity and isotacticity of polymeric chains. After grafting, it is observed in Figure 11b that rr extent decreases from 0.284 to 0.235. In fact grafting tendency exists among those structures with 1,2-vinyl units in the form of rr sequences. Based on the NMR results, we proposed the following mechanism:



Scheme VII. Proposed mechanism of grafting polystyrene on 1,2 polybutadiene

CONCLUSION

Solution polymerization of styrene in the presence of low molecular weight PBD gave higher grafting degree while inhibiting gel formation. Liquid NMR was used to study and determine both qualitatively and quantitavely the mechanism and extent of grafting. By fraction precipitation with appropriate solvents PS homopolymer and ungrafted PBD are removed from grafted PBD. ^{13}C NMR study on the grafted samples showed that there is no olefinic or aliphatic quaternary carbon formation. This excludes abstraction mechanism at low or high temperature thermal polymerization of styrene in the presence of PBD and only addition reactions contribute to the grafting. Moreover, it was shown that *cis* and *trans* isomers have equal grafting activity and higher temperature contributed to higher grafting rate while it caused moderate increase in grafting extent. Based on the obtained NMR results, an addition mechanism is proposed in which grafting occurs among syndiotactic rr sequences of 1,2-PBD.

ACKNOWLEDGEMENT

The authors wish to acknowledge NPC-rt for the financial support of this work.

REFERENCES

1. Manaresi P, Passalacqua V, Pilati F, Kinetics of

graft polymerization of styrene on cis-1,4-polybutadiene, *Polymer*, **16**, 520-526, 1975.
2. Gasperowicz A, Taskawaski W, Grafting of styrene onto low molecular weight polymers and copolymers of butadiene, *J Polym Sci, polym Chem Ed*, **14**, 2875-2886, 1976.
3. Schellenberg J, Hamman B, On the graft polymerization of styrene and acrylonitrile onto polybutadiene in the presence of vinyl acetate. I. Preparation of graft polymers, *J Appl Polym Sci*, **45**, 1425-1430, 1992.
4. Schellenberg J, Hamman B, On the graft polymerization of styrene and acrylonitrile onto polybutadiene in the presence of vinyl acetate. II. Properties of graft polymers, *J Appl Polym Sci*, **45**, 79-84, 1992.
5. Estenoz DA, Meira GR, Grafting of styrene onto polybutadiene: Calculation of the molecular macrostructure, *J Appl Polym Sci*, **50**, 1081-1098, 1993.
6. Hazar B, Kurt A, Polymerization kinetics of styrene by oligododecandioyl peroxide, and its use in the preparation of graft copolymers, *Eur Polym J*, **31**, 499-503, 1995.
7. Fischer M, Hellmann GP, On the evolution of phase patterns during the high-impact-modified polystyrene process, *Macromolecules*, **29**, 2498-2509, 1996.
8. Braun D, Fischer M, Kozera A, Bigraft terpolymers with polybutadiene backbone and styrene as well as methyl methacrylate grafts, *Eur Polym J*, **12**, 791-800, 1996.
9. Estenoz DA, Valdez E, Oliva H, Meira GR, Bulk polymerization of styrene in the presence of polybutadiene: determination of the molecular structure, *J Appl Polym Sci*, **59**, 861-885, 1996.
10. Estenoz DA, Leal GP, Lopez YR, Oliva HM, Meira GR, Bulk polymerization of styrene in the presence of polybutadiene. The use of bifunctional initiators, *J Appl Polym Sci*, **62**, 917-939, 1996.
11. Textle HM, Saenz MEDL, Putaux JL, Valle LFRD, Santos RG, Nanodispersion of polybutadiene in polystyrene through controlled "grafting from" free radical polymerization using a diphenylmethyl type radical, *Macromolecules*, **31**, 2696-2698, 1998.
12. Estenoz DA, Gonzalez IM, Oliva HM, Meira GR, Polymerization of styrene in the presence of polybutadiene: determination of the molecular structure, *J Appl Polym Sci*, **74**, 1950-1961, 1999.
13. Soto G, Nava E, Rosas M, Fuenmayor M, Gonzalez IM, Meira GR, Oliva HM, Bulk polymerization of styrene in the presence of polybutadiene: Effect of initiator type and prepolymerization conditions on particle morphology, *J Appl Polym Sci*, **92**, 1397-1412, 2004.
14. Casis N, Estenoz DA, Gugliotta L, Oliva HM, Meira GR, Heterogenous bulk polymerization of styrene in the presence of polybutadiene: Calculation of the macromolecular structure, *J Appl Polym Sci*, **99**, 3023-3039, 2006.
15. Casis N, Luciani CV, Estenoz DA, Martinelli M, Strumia M, Meira GR, Partition of tert-dodecyl mercaptan in systems containing styrene, polystyrene, and polybutadiene: Its effect on the macromolecular characteristics of high-impact polystyrene, *e-Polymers*, 085, 2007.
16. Brydon A, Burnett GM, Cameron GG, Free-radical grafting of monomers to polydienes. I. Effect of reaction conditions on grafting of styrene to polybutadiene, *J Polym Sci, Polym Chem Ed*, **11**, 3255-3269, 1973.
17. Huang NJ, Sundberg DC, Fundamental studies of grafting reactions in free radical copolymerization-I: A detailed kinetic model for solution polymerization, *J Polym Sci Part A, Polym Chem*, **33**, 2533-2549, 1995.
18. Huang NJ, Sundberg DC, Fundamental studies of grafting reactions in free radical copolymerization. II. Grafting of styrene, acrylate, and methacrylate monomers onto cis-polybutadiene using AIBN initiator in solution polymerization, *J Polym Sci Part A, Polym Chem*, **33**, 2551-2570, 1995.
19. Huang NJ, Sundberg DC, Fundamental studies of grafting reactions in free radical copolymerization. III. Grafting of styrene, acrylate, and methacrylate monomers onto cis-polybutadiene using benzoyl peroxide initiator in solution polymerization, *J Polym Sci Part A, Polym Chem*, **33**, 2571-2586, 1995.
20. Huang NJ, Sundberg DC, Fundamental studies of grafting reactions in free radical copolymerization-IV: Grafting of styrene, acrylate, and

methacrylate monomers onto vinyl-polybutadiene using benzoyl peroxide and AIBN initiators in solution polymerization, *J Polym Sci Part A, Polym Chem*, **33**, 2587-2603, 1995.
21. Liu S, Huang B, Synthesis of a novel graft-like copolymer of syndiotactic polystyrene with polybutadiene, *Macromol Rapid Commun*, **20**, 484-486, 1999.
22. Golub MA, Thermal rearrangements of polybutadienes with different vinyl contents, *J Polym Sci, polym Chem Ed*, **19**, 1073-1083, 1981.
23. Grassie N, Development in Polymer Degradation-4, ch 2, Golub MA, *Thermal rearrangements of unsaturated hydrocarbon polymers*, Applied Science, 1982.
24. Peng FM, Polybutadiene grafting and crosslinking in high impact polystyrene bulk thermal process, *J Appl Polym Sci*, **40**, 1289-1302, 1990.
25. Aerdts AM, de Krey JED, Kurja J, German AL, Emulsifier free grafting of styrene and methyl methacrylate concurrently onto polybutadiene and determination of the copolymer microstructure, *Polymer*, **35**, 1636-1647, 1994.
26. Aerdts AM, Theelen SJC, Smit TMC, German AL, Grafting of styrene and methyl methacrylate concurrently onto polybutadiene in semi-continuous emulsion processes and determination of copolymer microstructure, *Polymer*, **35**, 1648-1653, 1994.
27. Pentimalli M, Capitani D, Ferrando A, Ferri D, Ragni P, Serge AL, Gamma irradiation of food packaging materials: An NMR study, *Polymer*, **41**, 2871-2881, 2000.
28. Ziaie F, Noori A, Anvari F, Ghaffari M, Ahmadian V, Durrani SA, Effect of high-dose electron irradiation on specific heat capacity of high-impact polystyrene, *Rad Measure*, **40**, 758-761, 2005.
29. Fischer JP, Kinetik der radikalischen pfropfung von styrol auf polybutadiene, *Angew Makromol Chem*, **33**, 35-74, 1973.
30. Crompton TR, Reid VW, Unsaturation in high impact polystyrene analytical studies, *J Polym Sci, polym Chem Edn*, **1**, 347-355, 1963.
31. Bovey F, Nuclear Magnetic Resonance Spectroscopy, Bell Telephone Laboratories, 1988.
32. Tonelli A, NMR Spectroscopy and Polymer Microstructure, VCH, 1989.
33. Pham Q, Petiaud R, Watson H, Darricades MFL, Proton and Carbon NMR Spectra of Polymers, Penton, London, 1991.
34. Randall JC, Polymer Sequence Determination Carbon-^{13}C NMR Method, Academic, 1977.
35. Lacoste J, Delor F, Pilichowski JF, Singh RP, Vishwa Prasad A, Sivaram S, Polybutadiene content and microstrusture in high impact polystyrene, *J Appl Polym Sci*, **59**, 953-959, 1996.
36. Lin CT, Liu MC, Studies on the graft polymerizations of styrene and methyl methacrylate to hydroxyl terminated polybutadiene, *J Polym Res*, **2**, 127-132, 1995.
37. Sadeghi GMM, Barikani M, Morshedian J, Taromi FA, Determination of microstructure of polybutadiene-ol backbone by FTIR and NMR spectroscopy, *Iran Polym J*, **12**, 515-521, 2003.
38. Allen SG, Bevington JC, Comprehensive Polymer Science, vol. 6, ch 14, Platt AE, *Rubber modification of plastics*, 437-449, Pergamon, 1989.
39. Husain A, Hamielec AE, Thermal polymerization of styrene, *J Appl Polym Sci*, **22**, 1207-1223, 1978.
40. Liaw DJ, Lin LL, Studies on graft copolymerization of cyclohexyl methacrylate onto 1,2-polybutadiene, *J Appl Polym Sci*, **37**, 1993-2006, 1989.
41. Brydon A, Burnett GM, Cameron GG, Free-radical grafting of monomers to polydienes. II. Kinetics and mechanism of styrene grafting to polybutadiene, *J Polym Sci, Polym Chem Ed*, **12**, 1011-1021, 1974.
42. Mochel D, Carbon-13 NMR of polybutadiene, *J Polym Sci A-1*, **10**, 1009-1018, 1972.
43. Kumar D, Rao MR, Rao KVC, Carbon-13 NMR of 1,2-polybutadiene: configurational sequencing, *J Polym Sci Polym Chem Edn*, **21**, 365-373, 1983.
44. Ziaee F, Salehi Mobarake H, Nekoomanesh M, Arabi H, Study of tacticity and thermal rearrangement of low molecular weight 1,2- polybutadiene by NMR, *e-Polymers*, 2008, (in press).