

Polystyrene Grafted to ABS Backbone by Living Radical Polymerization With TEMPO

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ABSTRACT

A stable free radical (2,2,6,6-tetramethylpiperidiny-1-oxy, TEMPO) polymerization technique was applied to a graft polymerization of styrene (St) to acrylonitrile-butadiene-styrene terpolymer (ABS). Initially the adduct 1-benzoyl-2-phenyl-2-(2',2',6',6'-tetramethyl-piperidiny-1'-oxy) ethane (Bz-TEMPO) was obtained by reacting benzoyl peroxide, styrene, and TEMPO and the product was isolated, characterized and hydrolyzed to the corresponding 1-hydroxyl derivative (HO-TEMPO). The hydroxyl product (HO-TEMPO) that contains a primary hydroxyl group was coupled with brominated ABS (ABS-Br) to yield the macroinitiator ABS (ABS-TEMPO). This macroinitiator was used to prepare the controlled graft copolymer PS-*g*-ABS by "living" free radical polymerization of styrene onto ABS. The product was purified and identified by ¹H NMR and IR spectroscopy.

Key Words:

ABS;
living radical polymerization;
TEMPO;
graft copolymerization.

INTRODUCTION

Several reports have recently appeared on the subject of grafting of vinyl monomers onto acrylonitrile-butadiene-styrene (ABS) terpolymer. Abdel-Razik has studied grafting of acrylamide onto ABS using ultraviolet light in the presence of benzophe-

none to form the radical site at which initiation may proceed [1]. Wilkie et al. [2] have utilized the Geusken's procedure [3,4] the anthracene-sensitized formation of hydroperoxide, for the grafting of methacrylic acid [5], acrylamide [5], and acrylic

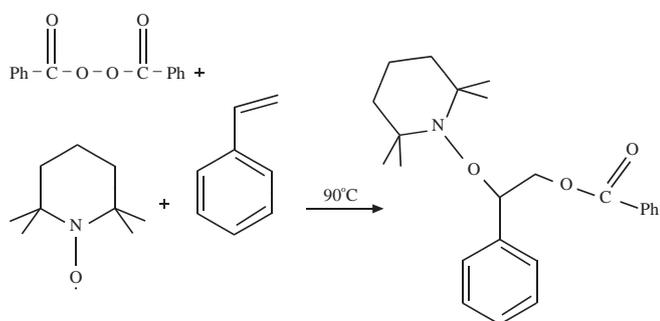
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acid[6] onto ABS.

The development of living free-radical polymerization for the preparation of polymers with controlled molecular weight and narrow polydispersity is among the most significant accomplishments in polymer synthesis [7,8]. One technique for performing such chemistry involves the use of 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) as a chain-end counter-radical to mediate the polymerization of styrene and styrenic derivatives.

Nitroxide mediated polymerization method is a controlled free radical methodology, which allows the synthesis of star and graft copolymers with controlled molecular weights under mild conditions. This new polymerization method is based on the use of traditional radical initiator (for example, B.P.O) in presence of stable nitroxide radical (for example, TEMPO). Graft copolymerization of vinyl monomer onto plastics in homogeneous media is one way to modify and enlarge the range of useful plastics. Compared with other graft copolymerization, an advantage of living free radical polymerization is that in the preparation of grafted copolymers, the terminal group of (the initial graft segments, e.g. nitroxide groups, are stable in air at room temperature, and prepolymers can be isolated, stored and used as needed, and less stringent polymerization conditions are required.

In the present study, living free radical polymerization has been investigated for synthesizing PS-g-ABS copolymer using the concept of M.K. Georges and coworker [18] and the methodology developed by C.J. Hawker and J.L. Hedrick [13,17]. Thus, 1-benzoyl-2-phenyl-2-(2',2',6',6'-tetramethyl-piperidinyl-1'-oxy)ethane (Bz-TEMPO) is synthesized (Scheme I) and hydrolyzed to the corresponding 1-hydroxyl derivative (HO-TEMPO) (Scheme II). This functional



Scheme I. Synthesis of Bz-TEMPO.

nitroxyl compound is coupled with brominated ABS according to Scheme III. The resulting macroinitiator (ABS-TEMPO, Scheme IV) for living free radical polymerization is then heated in the presence of styrene (Scheme V) for formation of controlled grafting onto ABS.

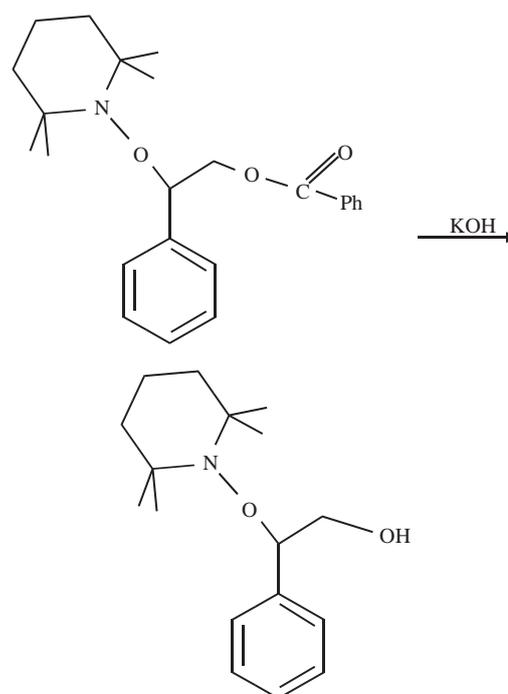
EXPERIMENTAL

Materials

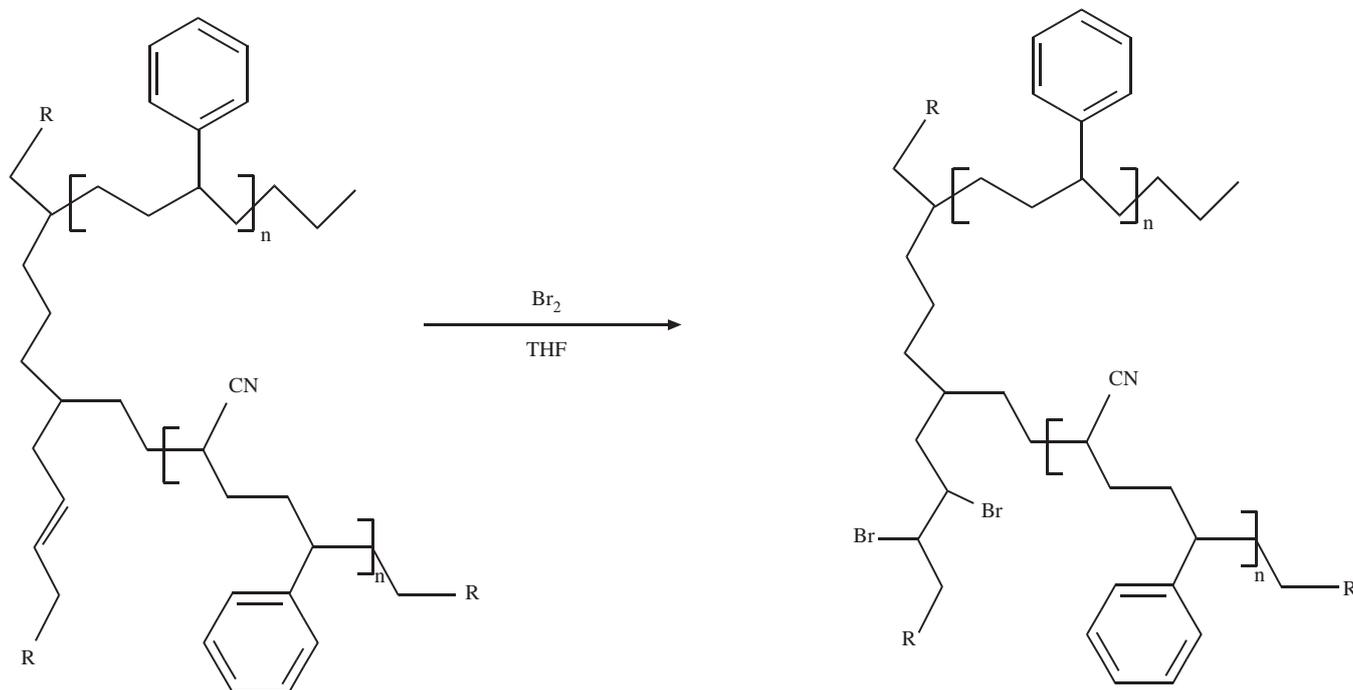
ABS was obtained from Kumho, Kore. According to IR spectroscopy, ABS contains 11.5% butadiene units, 63% styrene units and 25.5 % acrylonitrile [10]. TEMPO was prepared by the method reported previously [11]. Benzoyl peroxide (BPO) was precipitated from chloroform into methanol and then recrystallized at 0 C. Styrene (Fluka) was distilled under reduced pressure. THF (Merck) was distilled from sodium/benzophenone. Acetone, calcium chloride, ammonium chloride, *para*-nitrotoluene, hydrazine hydrate and solvents were purchased from Merck and used without further purification.

Instrumentation

¹H NMR Spectra were recorded with FT-NMR (400



Scheme II. Synthesis of BS or HO-TEMPO.



Scheme III. Bromination of ABS.

MHz) Bruker in CDCl_3 . Analytical TLC was performed on commercial Merck plates coated with silica gel GF254 (0.25 mm thick). IR Spectra were measured with Shimadzu Model IR-408 spectrometer.

Complete Bromination of ABS

The bromination reaction was carried out in 100 mL tetrahydrofuran solution at 0 C. 4 mL Bromine (0.5 mol) needed for a bromination of the ABS, was added dropwise into 0.5 g polymer solution [12]. The solution was stirred for 30 min, after all the bromine had been added. The solution was then poured into 100 mL of methanol. The precipitated polymer was filtered and washed with methanol and dried at vacuum oven. Operation was carried out under exclusion of any oxygen whenever possible. The polymer obtained weighed 0.6 g.

Synthesis of 1-(Benzyloxy)-2-phenyl-2-(2',2',6',6'-tetramethyl-1'-piperidinyloxy) ethane (Bz-TEMPO)

To a solution of benzoyl peroxide (4.0 g, 12.4 mmol) in distilled styrene (160 mL) was added 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)(5.68 g, 36.4 mmol), and the solution was heated at 80 C under nitrogen for 20 h.

After cooling, the solution was evaporated to dry-

ness and purified by column chromatography eluting with 1:1 hexane/dichloromethane, gradually increasing to 1:9 hexane/dichloromethane to give the modified TEMPO initiator (Bz-TEMPO) as a pale yellow oil (2.64 g, 42%)

$^1\text{H NMR}$ (CDCl_3) δ = 0.75, 1.07, 1.21, 1.37 (12H, CH_3), 1.38-1.52 (6H, CH_2), 4.53 (j = 6Hz, 1H, CHH), 4.83 (j = 6Hz, 1H, CHH), 5.06 (j = 3Hz, 1H, CH), 7.25-7.56 8H, ArH), 7.91(j = 6Hz, 2H, ArH)(Figure 1) (Scheme I)

Synthesis of 1-Hydroxy-2-phenyl-2-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethane (HO-TEMPO)

To a solution of the benzyl ester (Bz -TEMPO)(3.2 g, 8.4 mmol) in ethanol (100 mL) aqueous sodium

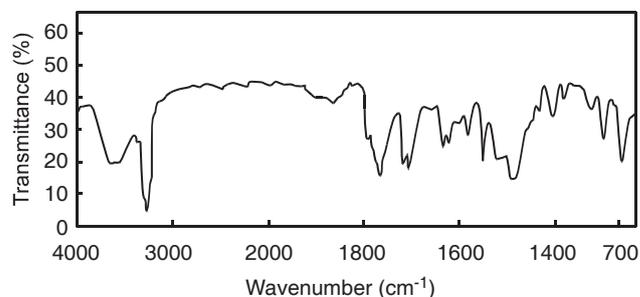


Figure 1. IR Spectroscopy of Bz-TEMPO.

hydroxide (10 mL of 1N solution, 10 mmol) was added, and the solution was heated at reflux under nitrogen for 2 h. After cooling, the solution was evaporated to dryness and partitioned between water (200 mL) and dichloromethane (200 mL). Then the aqueous layer was extracted with dichloromethane (2×100 mL), and with the combined organic layer were dried with magnesium sulphate and evaporated to dryness. The crude product was purified by column chromatography eluting with 1:4 hexane/dichloromethane, gradually increasing to 1:9 hexane/dichloromethane to give the hydroxy derivative (HO-TEMPO) as a pale yellow oil (2.01 g, 87%).

IR spectroscopy: 3300 cm^{-1} - 3600 cm^{-1} for the O-H bond, 1000 cm^{-1} - 1260 cm^{-1} for the C-O bond, 2962 cm^{-1} - 2872 cm^{-1} for the CH_3 stretching bond, 1375 cm^{-1} , 1450 cm^{-1} for the CH_3 vibration bond [13] (Figure 1 and Scheme II).

Preparation of the Alkoxy Amine Based on ABS (ABS-TEMPO)

To a 250 mL three-necked flask was added a solution of hydroxy-functionalized initiator (HO-TEMPO) (20 mg) in 5 mL THF and NaH (3 mg, 60% dispersion in oil). The reaction mixture was stirred for 20 min under argon, and brominated ABS (300 mg), dissolved in dry THF (5 mL), was added dropwise. The reaction was then heated at reflux under argon for 12 h, cooled, and evaporated to dryness. The residue was redissolved in THF (20 mL) and precipitated in the solution of 8:2

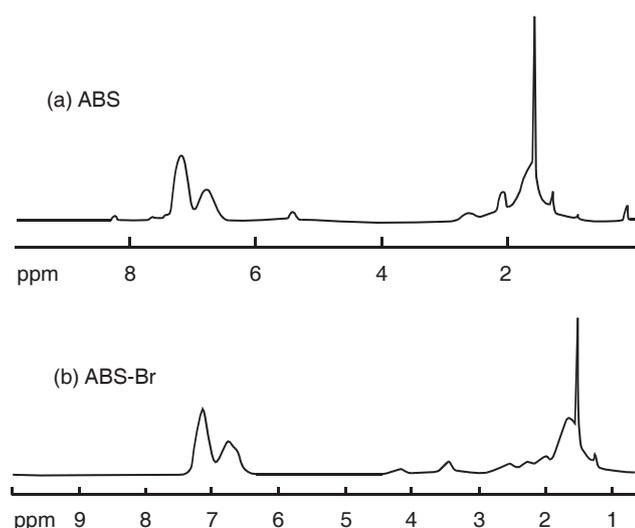


Figure 2. ^1H NMR Spectrum of ABS (a) and ABS-Br (b).

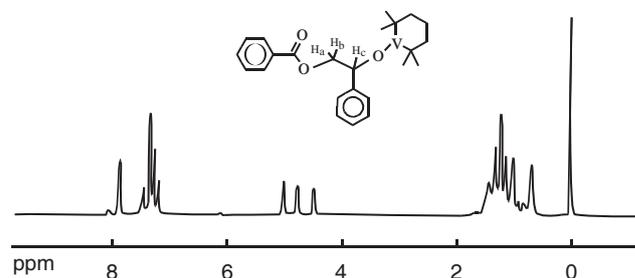


Figure 3. ^1H NMR Spectrum of Bz-TEMPO

methanol/water (100 mL) to give the TEMPO-functionalized polymer as a white solid (310 mg). The product structure was ABS-TEMPO according to ^1H NMR (Figure 2). ^1H NMR (400 MHz, CDCl_3): $\delta = 0.50$ - 1.91 ppm (aliphatic and TEMPO protons), 3.44, 4.17 ppm (CH_2 protons and CHBr protons), 5.25-5.77 ppm (vinyl protons), 7.23-7.42 (aromatic protons) (Figure 3) (Scheme IV).

Graft Copolymerization of Styrene onto ABS by ABS-TEMPO

A mixture of styrene (1.88 g, 18 mmol) and the TEMPO functionalized ABS (ABS-TEMPO)(0.0394g) were placed in a glass ampoule. After three freeze-thaw cycles, the glass ampoule was sealed-off from the vacuum line and placed in an oil bath at 125 C for 3 h. The resulted copolymer was dissolved in toluene and precipitated in methanol twice. The separation of PS-g-ABS from PS (probably thermally formed) was carried out partly according to a procedure given by Xie and coworkers [14]. Thus the crude product was extracted with cyclohexane at 30 C three times in order to remove polystyrene. The controlled graft copolymer was obtained as a white solid in 20% yield. ^1H NMR (CDCl_3): $\delta = 1.42$ - 1.83 ppm (aliphatic protons of polystyrene), 6.45-7.23 ppm (aromatic protons of polystyrene and macroinitiator), 7.30-7.42 ppm (phenyl protons of macroinitiator)(Figure 4 and Scheme V).

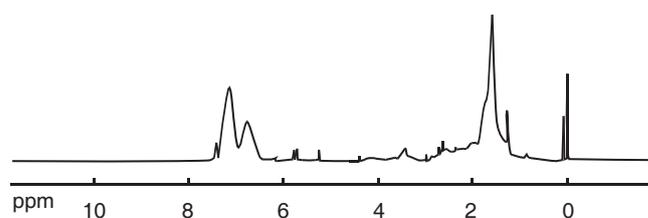
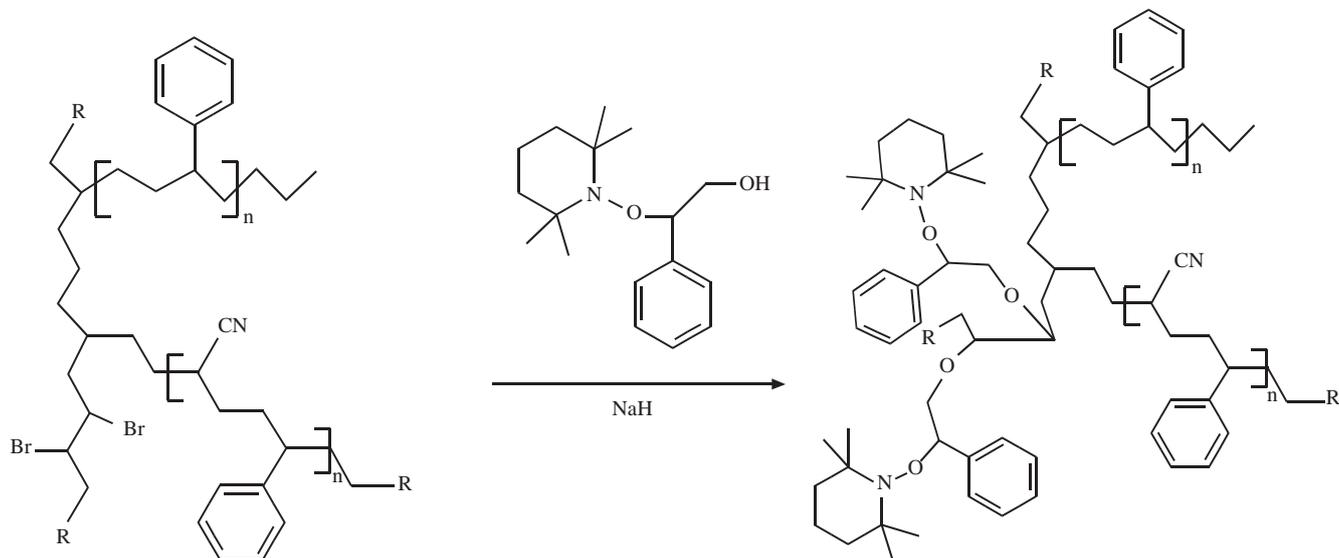


Figure 4. ^1H NMR Spectrum of macroinitiator ABS-TEMPO.



Scheme IV. Synthesis of macroinitiator ABS-TEMPO.

RESULTS AND DISCUSSION

Bromination of ABS

Since in the styrene-diene block copolymer the polydiene blocks are unsaturated, they can participate in many additional reactions like hydrogenation, halogenations, etc.

Bromine addition at the double bonds of polydiene blocks maybe interesting for at least two reasons: on one hand, styrene-diene block copolymers having brominated polydiene blocks (called brominated block copolymers) are useful intermediate materials for subsequent chemical reactions such as grafting or substitution reaction [15], the result of which are polymers with expected new properties as compared with base copolymer.

On the other hand, brominated block copolymers maybe important for a better understanding of the morphology of thermoplastic rubbers in general.

The bromine reacts with the polybutadiene block double bonds by addition and for every bromine molecular addition a double bond disappears. When we are

talking about polybutadiene block microstructure of brominated ABS, this is in fact when the bromination of ABS is not complete.

The brominated ABS copolymer was characterized by ^1H NMR spectroscopy (Figure 2a,b). The chemical shifts at 3.45-4.17 ppm represent the protons of CHBr corresponding to 1.4(cis, trans) or 1.2 unit in ABS copolymer, 1.25-2.55 ppm represent the aliphatic protons in ABS and those at 6.75-7.25 ppm the protons of aromatic (Scheme III and Figure 2a,b).

Unimolecular Initiators

Initially a bimolecular initiating system consisting of traditional radical initiator, such as benzoyl peroxide, in combination with TEMPO was introduced by Georges [18]. However, the difficulty in controlling chain ends, molecular weight, and macromolecular architecture for such systems forced us to consider alternatives, which provided better control over the polymeric structure. Inspired by the concept of well-defined initiating species in anionic polymerizations, a range of unimolecular initiators for living free radical systems were developed which offer a number of advantages over the traditional bimolecular mixtures [16]. The unimolecular initiators are all covalent adducts based on an alkoxyamine structure, which on decomposition gives an initiating benzylic radical and a nitroxide radical in the desired 1:1 stoichiometry. It has recently been

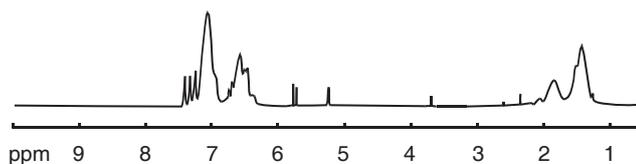
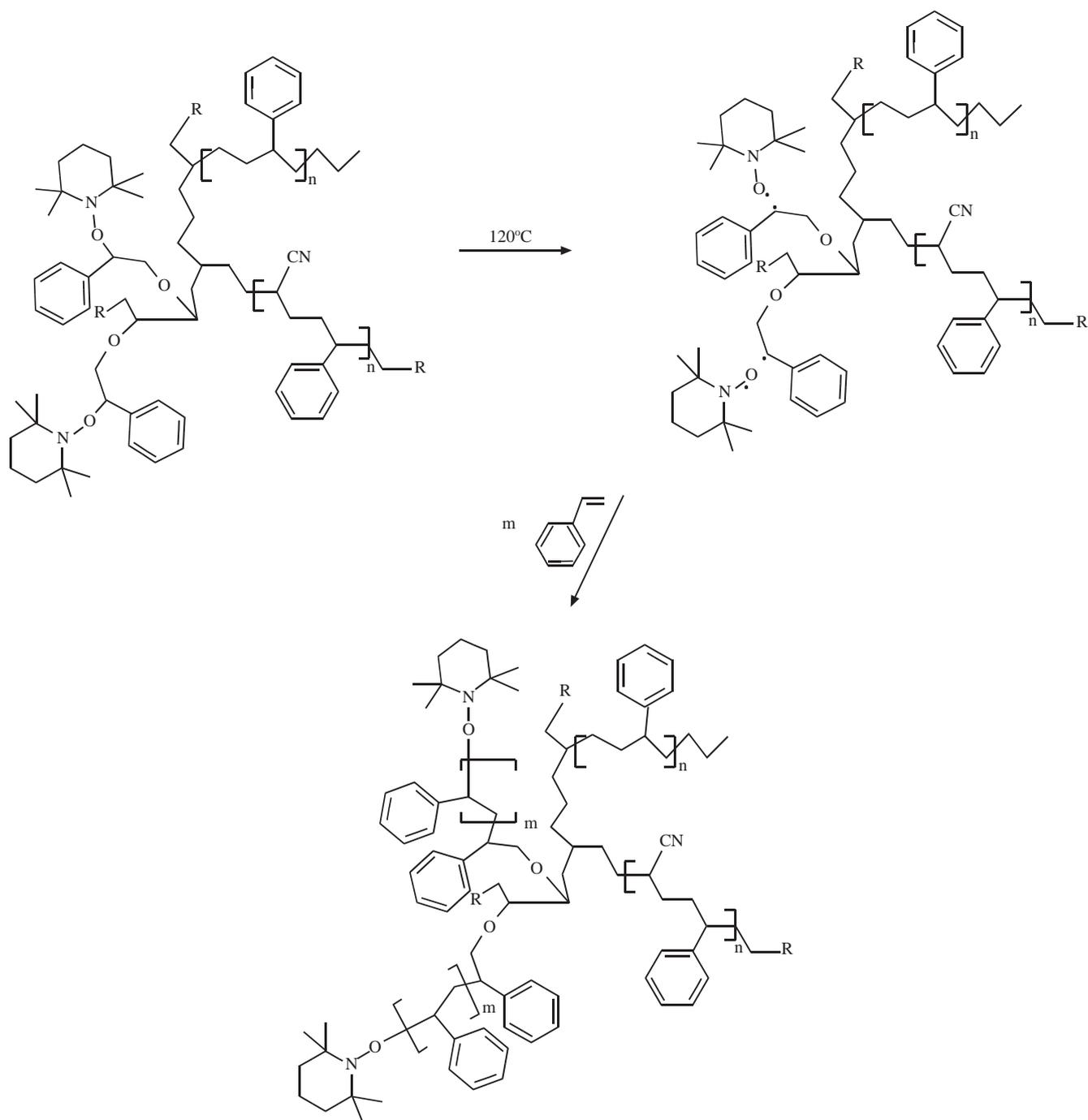


Figure 5. ^1H NMR Spectrum of SBR-g-PS.



Scheme V. Synthesis of controlled grafting onto ABS.

shown that the strength of the C-ON bond in alkoxyamine based unimolecular initiators is of crucial importance to the success of the living free radical process. If the C-ON bond is too thermally stable, then the homolysis is slow compared to propagation, leading to uncontrolled propagation, and broad polydisperse polymers are obtained [13]

Preparation of Alkoxyamine Based on ABS (ABS-TEMPO)

Bz-TEMPO was synthesized to optimize the yield performed under a variety of conditions where the ratio of TEMPO to BPO was varied and also the reaction temperature. However, under all conditions, the yield was

relatively low, no more than around 42%. The structure of the product was confirmed by ^1H NMR spectrum [9]. The hydrolysis of Bz-TEMPO gave a crude product from which the hydroxyl functional HO-TEMPO could be readily separated from unhydrolyzed Bz-TEMPO.

Thin layer chromatography (TLC) gave two spots on the silica gel sheets corresponding to Bz-TEMPO and HO-TEMPO. Purification of the crude product was performed by chromatography using a silica gel column. The purified product was identified as HO-TEMPO by ^1H NMR [17]. HO-TEMPO reacts with ABS-Br to give the macroinitiator ABS-TEMPO according to Scheme IV. The ^1H NMR spectrum of the macroinitiator is shown in Figure 4. Comparison with the ^1H NMR spectrum of ABS-Br indicates that in the reaction process, because the chemical shift of CH-O and CH-Br are similar, therefore, does not change in the chemical shift of CH-O, whereas, the functional group 2-phenyl-2-(2',2',6',6'-tetramethyl-piperidinyl-1'-oxy) ethoxy appears with characteristic signals at 1.03-1.58 ppm and 7.20-7.42 ppm. The thermal homolytic scission of the C-O bond of the aminoxy moiety of the ABS-TEMPO took place at 125 C and caused the radical polymerization of styrene to yield the controlled graft copolymer ABS-g-PS according to Scheme V. The bond dissociation is considered to be reversible. The crude polymerization product was purified as given in the experimental section. The yield of crude product corresponding to 56% was reduced to only 20% after purification. A large amount of homopolystyrene was produced which was isolated and identified by its ^1H NMR spectrum. ^1H NMR of the purified product (Figure 5) indicates the formation of graft copolymer ABS-g-PS, since the chemical shifts at 6.49-6.75 ppm, 7.03-7.41 ppm represent the aromatic protons of the oxyethylene repeat unit.

Both the yield of purified PS-g-ABS and homopolystyrene and ^1H NMR spectra indicate that thermal polymerization of styrene predominates the polymerization process. Thermal polymerization in connection with nitroxide free radical mediated polymerization of styrene, and the factor affecting alkoxyamine homolysis rates have been reported [18,19]. In the TEMPO mediated polymerization of styrene, it has been found that the polymerization is driven by a constant supply of initiating radicals by

thermal initiation to make up for the irreversible termination reactions while the adduct with TEMPO controls molecular weight and polydispersities by exchange reactions [20].

CONCLUSION

It should be apparent from the discussion above that the synthesis of well-defined graft copolymer with control over molecular weight of graft is feasible using nitroxide-mediated living free radical procedures. The versatility of this process is further enhanced by the compatibility of the alkoxyamine initiating units with a wide range of reaction conditions and functional groups.

In assessing the future of living free radical polymerization it should be noted that the field is a young and rapidly progressing area of research, and many of the difficulties or limitations associated with the general applicability of this technique are steadily, but surely, being overcome. The long-term goal of developing a new polymerization process which combines the best attributes of normal free radical polymerization with those of living anionic procedures is becoming a much more realistic possibility.

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Symbols and Abbreviations

ABS: Acrylonitrile butadiene styrene

TEMPO : 2,2,6,6-Tetramethylpiperidinyl-1-oxy

BPO: Benzoyl peroxide

St: Styrene

PS: Polystyrene

Br: Bromine

NMP: Nitroxide mediated polymerization

THF: Tetrahydrofuran

ATRP: Atom transfer radical polymerization

Bz-TEMPO: 1-benzoyl-2-phenyl-2-(2',2',6',6'-tetramethyl-piperidinyl-1'-oxy) ethane

BS-TEMPO or HO-TEMPO: 1-Hydroxy-2-phenyl-2-

(2',2',6',6'-tetramethyl-1'-piperidinyloxy) ethane
LFRP: Living free radical polymerization

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