Preparation of Diblock and Triblock Copolymers of Styrene, 2,5-Norbornadiene, Ethylmethacrylate and PEG by Nitroxide-controlled Free Radical Polymerization

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ABSTRACT

2,5-Norbornadiene has been polymerized in bulk at 125 °C in presence of a low molar mass of polystyrene-TEMPO as macroinitiator. The structure and polydispersity of the obtained diblock copolymer (PSt-PNB-TEMPO) were determined by IR, ^{1}H NMR spectroscopy and GPC measurement, respectively, where TEMPO is 2,2,6,6 tetramethylpiperidinyl-1-oxy and PNB is polynorbornadiene. The triblock copolymer of styrene-2,5-norbornadiene-ethylmethacrylate (PSt-PNB-PEMA) using a PSt-PNB-TEMPO as the macroinitiator in the presence of camphorsulphonic acid (CSA) was prepared. Also the triblock copolymer containing polyethylmethacrylate and poly(ethylene glycol) designated as PEMA-PEG-PEMA was synthesized by a novel method. The ^{1}H NMR and FTIR studies of triblock copolymers confirmed their structures and the absence of TEMPO end groups for PEMA.

INTRODUCTION

A number of workers have experimented, with reversible termination of chain growing polymer in free radical polymerization, pseudo-living polymers that are capable of stepwise chain growth [1–5]. The versatility of living ionic polymerizations is, however, limited by incompatibility of the growing chain ends (either anionic or cationic) with many different functional groups.

Synthetically demanding experimental require-

ments such as rigorous exclusion of water and oxygen and the use of ultra-pure reagents and solvents further reduce the general applicability of living anionic and cationic polymerizations to a narrow range of possible structures. Significant expertise is also demanded if the polymerizations are to be performed successfully.

Normal free radical polymerization is very limited in its utility for making polymers of controlled architecture because the initiation, propagation, and termination steps are simultaneous, which leads to a very broad polydispersity. Also, termination occurs

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by a variety of processes including radical coupling, and chain transfer to monomer, to solvent and to polymer chain having a variety of end group structures.
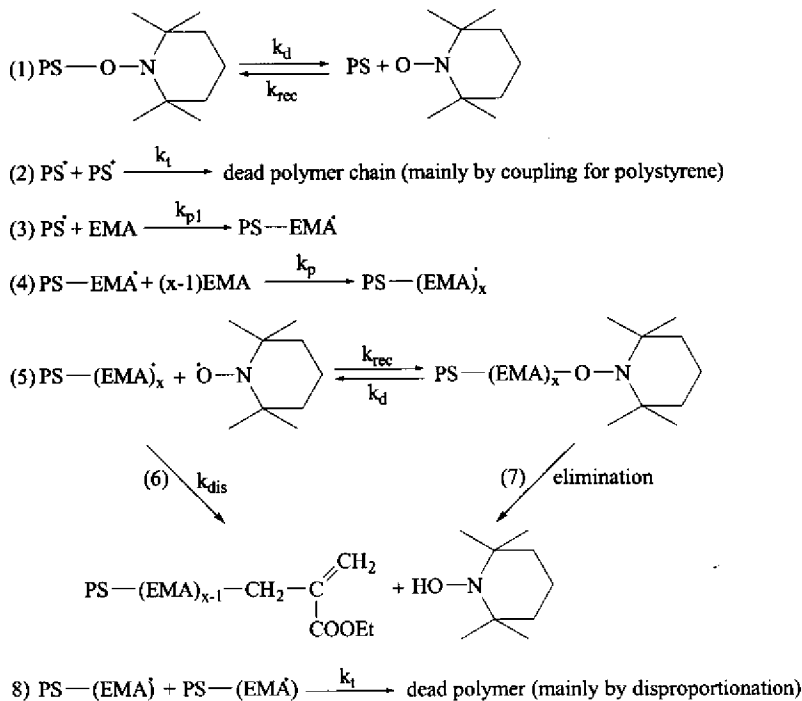
But in many respects, free radical procedures are the opposite of living ionic polymerizations since they are synthetically robust, compatible with a wide range of functional groups, but offer little or no control over macromolecular structure. Despite this drawback, free radical procedures are the main route to vinyl polymers and are of substantial economic importance. The development of a living free radical procedure, which combines the desirable attributes of traditional free radical systems with the desirable attributes of living polymerizations, would be a significant development in not only polymer synthesis, but also polymer science in general. The free radical polymerization mediated by stable nitroxyl radicals, such as 2,2,6,6-tetramethyl-piperidinyl-1-oxy (TEMPO), has been rapidly develop-

ed as a novel synthetic route to polymers with a narrow molecular weight distribution and an active chain end.

This approach has found unique and important applications in for example, random and block copolymerizations, suspension copolymerization and aqueous solution polymerization [6–15].

Several groups were investigated for free radical polymerization of acrylic monomers using macroinitiators[16–19].

In the case of nitroxide-mediated polymerization of methacrylic esters, low monomer conversion was always observed, because the formed alkoxyamines are totally converted after a short polymerization time into dead polymer chains by a β-hydrogen transfer reaction from the propagating radicals to TEMPO (also called disproportionation reaction). This reaction leads to the corresponding hydroxylamine and to an ω-unsaturated polymer (Scheme I) [20]. However,

(1) $PS—O—N$ $\underset{k_{rec}}{\overset{k_d}{\rightleftharpoons}}$ $PS + O—N$

(2) $PS^{\bullet} + PS^{\bullet}$ $\xrightarrow{k_t}$ dead polymer chain (mainly by coupling for polystyrene)

(3) $PS^{\bullet} + EMA$ $\xrightarrow{k_{p1}}$ $PS—EMA^{\bullet}$

(4) $PS—EMA^{\bullet} + (x-1)EMA$ $\xrightarrow{k_p}$ $PS—(EMA)^{\bullet}_x$

(5) $PS—(EMA)^{\bullet}_x + {}^{\bullet}O—N$ $\underset{k_d}{\overset{k_{rec}}{\rightleftharpoons}}$ $PS—(EMA)_x—O—N$

(6) k_{dis} (7) elimination

$PS—(EMA)_{x-1}—CH_2—C{\overset{CH_2}{\diagup}}$ $+$ $HO—N$
                                     $|$
                                     $COOEt$

8) $PS—(EMA)^{\bullet} + PS—(EMA)^{\bullet}$ $\xrightarrow{k_t}$ dead polymer (mainly by disproportionation)

Scheme I

except the end-group analysis by NMR spectroscopy, no report on a more thorough characterization of the polymers could be found in the literature. Livingness, in nitroxide-mediated polymerization of methacrylate derivatives, could only be achieved when those monomers were randomly copolymerized with a larger amount of styrenic monomer.

This technique was first reported by Hawker and was further applied for the synthesis of poly(styrene-*b*-(styrene-*co*-n-butyl methacrylate)) block copolymer.

The synthesis of block copolymers with polystyrene as a first block and the pure poly(methacrylic ester) as a second block was reported in two papers in which a TEMPO-capped polystyrene (PSt) was used as a macroinitiator. The first case concerned the methyl methacrylate polymerization [21]. The authors reported that initiation of this monomer at 125 °C by the TEMPO-capped polystyrene was only observed when reaction was carried out in the presence of camphorsulphonic acid; otherwise, no shift of the size exclusion chromatography peak could be seen. A bimodal molar mass distribution was obtained and it was explained by an incomplete initiation owing to the presence of dead polystyrene chains, the proportion of which increased when styrene conversion in the synthesis of the first block was increased. In the second case, (dimethylamino)ethyl methacrylate was polymerized to provide amphiphilic block copolymers with relatively narrow polydispersities ($\overline{M}_w / \overline{M}_n$ <1.3) [22].

Total consumption of the polystyrene macroinitiator was reported, but in contrast, monomer conversion was always incomplete, reaching its maximum value in less than 2 h at 125 °C. Poly(methacrylic ester) block length was shown to depend on the macroinitiator initial concentration; the lower the concentration, the longer the block length. Incomplete monomer conversion was explained by irreversible chain termination taking place after the propagation of a limited amount of monomer. However, the authors concluded that a better understanding of the polymerization mechanism was still needed. In both reported cases, polymerization of the methacrylate monomer was not of living type.

In this work PSt-PNB-TEMPO diblock copolymer using PSt-TEMPO as the macroinitiator was

prepared. PSt-PNB-PEMA Triblock copolymer using PSt-PNB-TEMPO as the macroinitiator in the presence of CSA was prepared. Also PEMA-PEG-PEMA triblock copolymer was synthsized by a novel method.

EXPERIMENTAL
Instrumental Measurements
FTIR Spectra were measured on a Shimadzu Model FTIR-8101M spectrometer. ^{1}H NMR Spectra were recorded on FT-NMR (400 MHz) Brucker in CDCl$_3$. The molecular weight of the resulting polymers was obtained with a maxima 820 GPC analysis instrument using polystyrene (10^6, 10^5, 10^4 Å) calibration standards with a THF mobile phase at a flow rate of 1 mL/min and column temperature at 50 °C.

Synthesis of TEMPO
TEMPO was prepared according to the Rauckman procedure [23]. Thus to 5g (0.027 mol) of 2,2,6,6-tetramethylpiperidine in a solution containing 50 mL of methanol, 3.5 mL of acetonitrile, 1.8 g of sodium hydrogen carbonate and 0.25 g of sodium tungstate was added 20 mL of 30 % hydrogen peroxide over 30 min. The mixture was allowed to stand at 30 °C for 3 days. At this point, the mixture was filtered and the filtrate was diluted with 200 mL of saturated sodium chloride solution. The pH was adjusted to 3–4 with dilute hydrochloric acid and the aqueous solution was extracted exhaustively with ether. The ether solution was dried over anhydrous magnesium sulphate and evaporated to give 4.5 g (85 %) of the desired product.

Synthesis of (Bz-TEMPO)
1-Benzyl-2-phenyl-2-(2′,2′,6′,6′-tetramethylpiperidin-yl-1-oxy)ether (Bz-TEMPO) was prepared by the following method proposed by Hawker [24]. Briefly, freshly distilled styrene, benzoyl peroxide (BPO) (64.61 g, 0.267 mol), and TEMPO (49.92 g, 0.32 mol) were charged in a glass ampoule, degassed, and sealed off under vacuum. The mixture was incubated at 90 °C for 3 h. After elimination of unreacted styrene the desired Bz-TEMPO could be separated as pale yellow oil by passing the reaction mixture through a column (φ=25 mm × 400 mm) packed with silica gel 60

(Merck) and eluting with a mixture of 1:100 (v/v) methanol/dichloromethane, gradually increasing to 2:100 (v/v) methanol/dichloromethane (30 % yield).

Synthesis of PSt-TEMPO

PSt-TEMPO was prepared by heating a mixture of Bz-TEMPO with a calculated amount of styrene at 130 °C under argon for 72 h [25].

Preparation of PSt-PNB-TEMPO

A mixture of low molar mass PSt-TEMPO (prepared by Bz-TEMPO using as the initiator) 45 mg, 2,5-norbornadiene (3 mL, 29.67 mmol), and camphor-sulphonic acid (38 mg, 0.163 mmol) was charged in a glass ampoule, degassed and sealed off under vacuum. The ampoule was stirred and heated in an oil bath at 125 °C for 32 h. Then the ampoule content was precipitated into methanol and the product was purified by dissolving in chloroform and reprecipitated into methanol for several times (30 % yield). The structure of obtained product was determined by ^{1}H NMR and FTIR spectra. FTIR: 3051–3030 (aromatic and vinylic C–H), 1726 (C=O of initiator), 1626–1950 (C=C of aromatic and vinylic segments).

Preparation of PSt-PNB-PEMA

A mixture of nitroxy-terminated PSt-PNB diblock copolymer (50 mg), ethylmethacrylate (2 mL, 15.96 mmol) and camphorsulphonic acid (38 mg, 0.163 mmol) was charged into a glass ampoule, degassed and sealed off under vacuum. The ampoule was stirred and heated in an oil bath at 130 °C for 5 h. Then the ampoule content was precipitated into methanol and the product was purified by dissolving in chloroform and reprecipitated into methanol then dissolving in chloroform and reprecipitated into petroleum ether for several times (20 % yield). The structure was PSt-PNB-PEMA according to ^{1}H NMR and FTIR: 2991–2937 (aliphatic C–H), 1734 (ester carbonyl).

Preparation of Chlorinated PEG

Chlorinated PEG (Cl–PEG–Cl) was prepared by the following method proposed by Geckeler [21]. Briefly HO–PEG–OH ($\overline{M}_n$ =6000) was chlorinated by the reaction with $SOCl_2$ in toluene solvent.

Preparation of Macroinitiator TEMPO-PEG-TEMPO

To a 250 mL three-necked flask was added NaH (48 mg, 2 mmol) and solution of HO-TEMPO (297 mg, 1 mmol) was prepared according to the method described previously [18] in 20 mL toluene. The solution was stirred and refluxed under nitrogen for 24 h. To this solution was added dropwise a Cl–PEG–Cl (150 mg, 0.25 mmol) solution in 20 mL toluene. Stirring and refluxing of the reaction mixture was continued for 24 h. Then, the solution was cooled, filtered and solvent was removed. A small amount of CH_2Cl_2 was added and the product was precipitated twice in 500 mL ethanol from the CH_2Cl_2 at 4 °C.

The structure of obtained product was TEMPO-PEG-TEMPO according to ^{1}H NMR and FTIR investigation (60 % yield). FTIR study indicated peak for C=C of aromatic segments at 1634–1472 cm^{-1}.

Preparation of PEMA-PEG-PEMA Triblock Copolymer

A mixture of TEMPO-PEG-TEMPO as macroinitator (100 mg, 0.0166 mmol), ethylmethacrylate (2 mL, 16.14 mmol), and camphorsulphonic acid (30 mg, 0.129 mmol) was charged into a glass ampoule, degassed and sealed off under vacuum. The ampoule was stirred and heated in an oil bath at 130 °C for 2 h. Then the ampoule content was precipitated into petroleum ether.

The crude product was dried in a vacuum oven at room temperature for 5 h. The crude product was dissolved in a small amount of $CHCl_3$ and precipitated in 200 mL ethanol at 4 °C for several times (40 % yield). The structure of obtained product was determined by ^{1}H NMR and FTIR spectroscopy. IR: 2937–2878 (aliphatic C–H), 1734 (ester carbonyl), 1626–1456 (C=C of aromatic segments and PEMA) and 1117 (C–O bond).

RESULTS AND DISCUSSION

Bz-TEMPO was synthesized to optimize the yield

125 °C
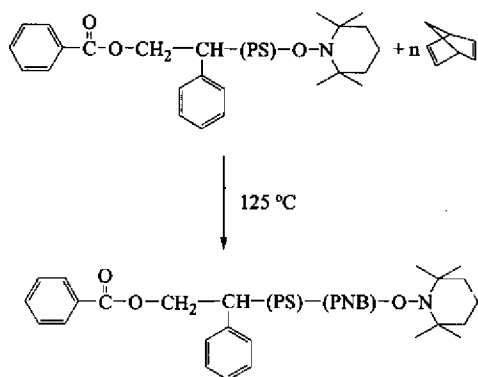
Scheme II

obtained under a variety of conditions where the ratio of TEMPO to BPO and styrene were varied as well as the reaction temperature. However, under all conditions, the yield was relatively low, being around 30 %.

Scission of C–O bond of the aminoxy moiety of the Bz-TEMPO took place at 125 °C and caused

the radical polymerization of vinylic monomers.

The polymerization of norbornadiene (NB) was carried out in absence and presence of camphorsulphonic acid using PS-TEMPO as the macro-initiator to yield PS-PNB-TEMPO diblock copolymer (Scheme II), the yield of polymerization of NB in the presence of camphorsulphonic acid (30 % yield) was higher than the polymerization of NB in the absence of camphorsulphonic acid (8 % yield).

Also the peaks at 6.3–7.5 ppm in ^{1}H NMR spectra (Figure 1) showed vinylic C–H of NB and aromatic C–H of PS, chemical shifts at 0.2–1.1 ppm represent the protons of TEMPO groups and chemical shifts at 0.5–2.5 ppm represent the protons of PNB. Gel permeation chromatography (GPC) was used for the determination of the average molecular weight of PS-PNB-TEMPO ($\overline{M}_n$=2128 and poly-dispersity, PD=1.2).

The thermal homolytic scission of the C–O bond of the aminoxy moiety of the nitroxy-terminated PS-PNB took place at 125 °C and caused the radical polymerization of EMA to yield the triblock
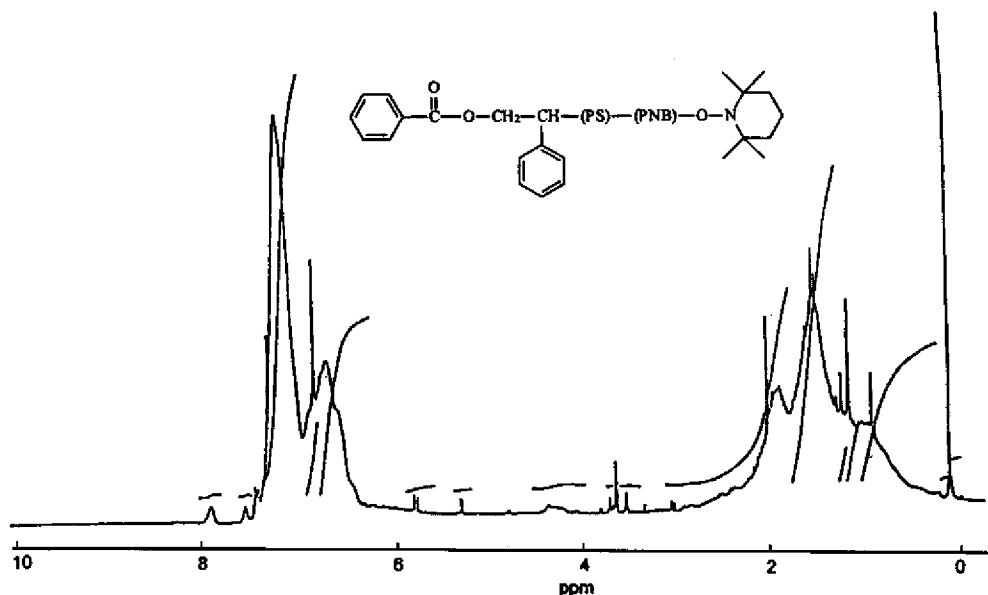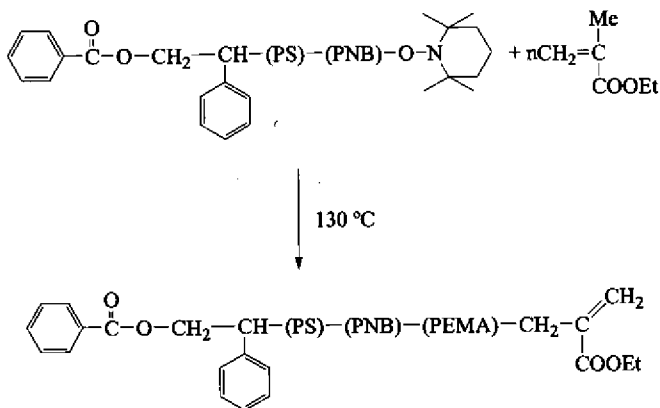

Figure 1. ^{1}H NMR Spectrum of PS-PNB-TEMPO in CDCl₃.

Scheme III

copolymer PS-PNB-PEMA according to Scheme III.

Formation of PSt-PNB-PEMA triblock copolymer using PS-PNB-TEMPO as the macroinitiator represent living property of PS-PNB diblock copolymer.

^{1}H NMR Spectrum of the purified copolymer (Figure 2) indicates the formation of triblock copolymer PS-PNB-PEMA, chemical shifts at 0.5-2 ppm represent the aliphatic protons in PS-PNB-PEMA, chemical shifts at 4.0 ppm represent the protons of $-OCH_2-$ group in PEMA and chemical shifts at 6.4-7.2 ppm represent aromatic C–H in PS and chemical shifts at 5.4 and 6.2 display vinylic C–H end of the PEMA.
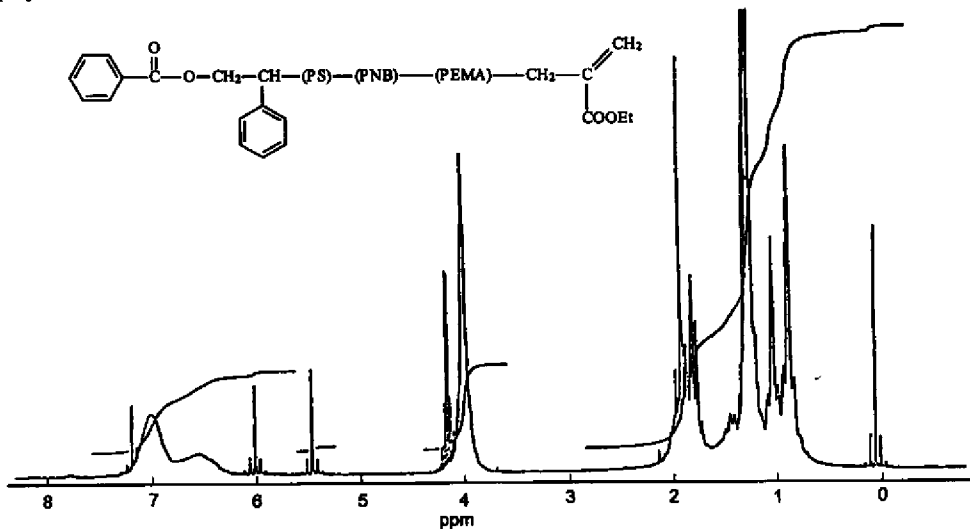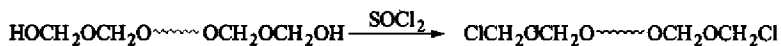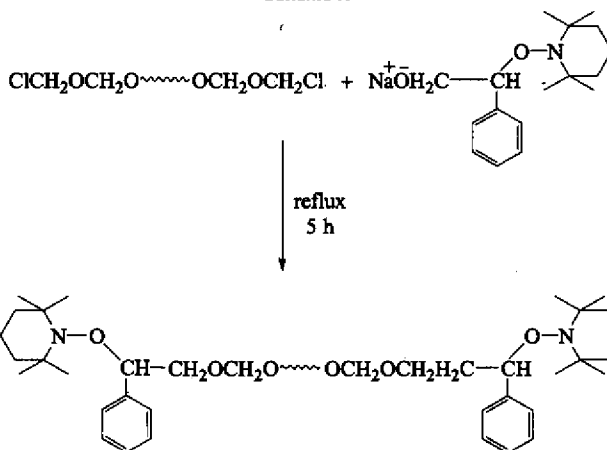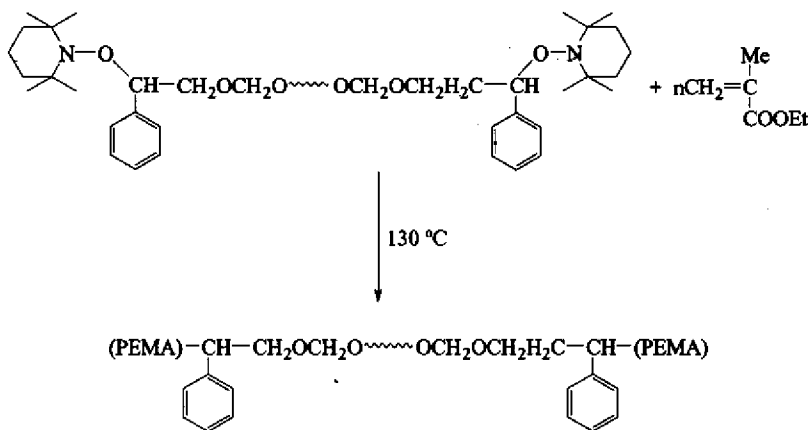
PEG was chlorinated using $SOCl_2$ in toluene

Figure 2. ^{1}H NMR Spectrum of PS-PNB-PEMA in CDCl₃.

$$HOCH_2OCH_2O\text{～～}OCH_2OCH_2OH \xrightarrow{SOCl_2} ClCH_2OCH_2O\text{～～}OCH_2OCH_2Cl$$

Scheme IV

$$ClCH_2OCH_2O\text{～～}OCH_2OCH_2Cl + Na\overset{+}{O}\overset{-}{H_2}C\text{—}CH\text{（TEMPO）}$$

reflux
5 h

Scheme V

$$\text{（TEMPO-N–O）}CH\text{—}CH_2OCH_2O\text{～～}OCH_2OCH_2H_2C\text{—}CH\text{（O–N-TEMPO）} + nCH_2{=}C\overset{Me}{\underset{COOEt}{}}$$

130 °C

$$\text{(PEMA)}\text{—}CH\text{—}CH_2OCH_2O\text{～～}OCH_2OCH_2H_2C\text{—}CH\text{—(PEMA)}$$

Scheme VI

solvent according to Scheme IV. PEG Macroinitiator was prepared through reaction between Cl–PEG–Cl and anion of HO-TEMPO (Scheme V). The expended small peaks in ^{1}H NMR spectra (Figure 3) at 0.5–2.1 ppm, 7.2–7.4 ppm indicate TEMPO group and aromatic unit and chemical shifts at 3.8–3.9ppm show C–H of PEG. The FTIR spectra (1634–1472 cm^{-1} aromatic unit and 970 cm^{-1} N–O bond) and absence of OH groups confirm the structure of TEMPO-PEG-TEMPO.

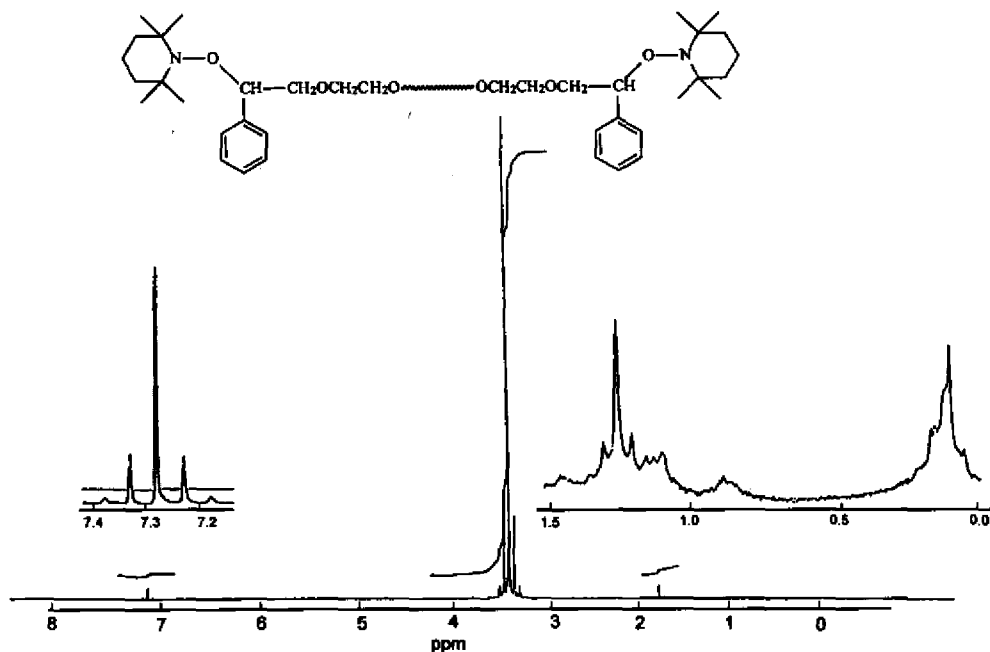**Figure 3.** ^{1}H NMR Spectrum of TEMPO-PEG-TEMPO in CDCl$_3$.

PEMA-PEG-PEMA Triblock copolymer was prepared by polymerization of EMA using TEMPO-PEG-TEMPO as the macroinitiator (Scheme VI). The reaction performed at bulk and toluene solvent in the presence of camphorsulphonic acid. The yield of polymerization at bulk was higher than toluene solvent.

^{1}H NMR Spectrum of PEMA-PEG-PEMA indicates the formation of this compound (Figure 4), the chemical shifts at 3.7–3.9 ppm represent the aliphatic protons in poly(ethylene glycol) and chemical shifts at 4.2 ppm represent the protons of –OCH$_2$– group in PEMA and also the aromatic segments peaks are presented at 7.2–7.4 ppm. On the other hand, the presence of bond at 1734 cm^{-1} (ester carbonyl) in FTIR spectra confirms the above structure.

All polymerizations were carried out in the presence of camphorsulphonic acid, to decrease the autopolymerization and increasing the yield of polymerization. A number of reaction accelerating additives have been developed which increase the rate of propagation for nitroxide mediated living free radical polymerization. This decreases the reaction time at elevated temperatures, which in turn leads to a smaller number of radical produced by autopolymerization. The addition of a small amount of an acylating species, such as camphorsulphonic acid, dramatically increases the rate of the polymerization such that conversion of ca. 90 % is reached within 4–5 h instead of 24 h.

The mechanism of action of these acylating agents may be co-ordination to the lone pair of the alkoxyamine-nitrogen resulting in more facile homolysis of the C–ON bond, or reaction of free nitroxide with the acylating agent resulting in a decrease in concentration of the mediating nitroxy radicals in the polymerization mixture [21].
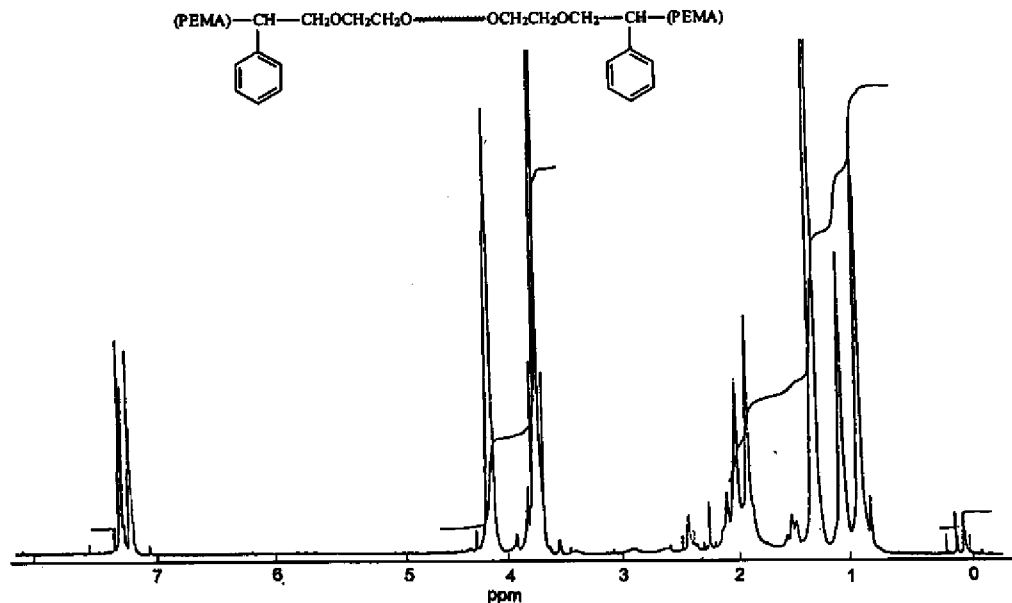
400

Figure 4. ¹H NMR Spectrum of PEMA-PEG-PEMA in CDCl₃.

CONCLUSION

The free radical polymerization of NB in the bulk at 125 °C, initiated by PS-TEMPO, proceeds in a living fashion resulting in narrow-polydispersity PNB. The bicyclo and tricyclo structures of PNB are determined by ¹H NMR and FTIR spectroscopy. Polymerization of EMA using PSt-PNB-TEMPO macroinitiator cofirmed the living properties of PSt-PNB polymer.

On the other hand, TEMPO-PEG-TEMPO macroinitiator was obtained with reaction between Cl–PEG–Cl and HO-TEMPO. PEMA-PEG-PEMA Triblock copolymer was prepared by free radical polymerization of EMA using TEMPO-PEG-TEMPO dinitroxide macroinitiator.

ACKNOWLEDGEMENTS

The authors like to express their gratitude to Ms. H.

Mivehchi for the linguistic corrections of the manuscript.

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