Polymer Bulletin 44, 261–268 (2000)

Polymer Bulletin

# Synthesis and characterization of *N*-phenylmaleimide-methylvinylisocyanate copolymers with polystyrene side chains

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Received: 6 October 1999/Revised version: 7 March 2000/Accepted: 7 March 2000

## Summary

*N*-Substitued maleimide-methylvinylisocyanate copolymers with high glass transition temperature ($T_g$) was prepared and reacted with 4-hydroxy TEMPO (4-hydroxy-2,2,6,6-tetramethyl piperidinoxy) to yield polymers possessing stable radical at the side chain. The resulting polymers behaved as polymeric counter radicals for the radical polymerization of styrene. Thus, stable free radical mediated polymerization at the side chain was achieved. The resulting graft copolymers were characterized by spectral and thermal analysis.

## Introduction

Design and synthesis of materials with novel properties is becoming an interestingly important aspect of polymer chemistry. Synthesis of polymers with controlled molecular architecture has been discussed due to the rising demands for the speciality polymers. Living polymerization is an essential technique for synthesizing polymers with controlled structure (narrow molecular weight distributions and controlled molecular weight). Living polymerization has largely been achieved using living anionic [1] and cationic [2,3] and group transfer [4] polymerization systems. From the practical point of view, however these techniques are less attractive than free radical polymerization, because the latter can be performed much more easily. The recent developments in controlled/living free radical polymerization have opened new pathways to prepare well-defined polymers also by radical mechanism. The most important controlled/living free radical polymerization methods are stable free radical polymerization (SFRP) [5-7], atom transfer radical polymerization (ATRP) [8-10] and reversible addition-fragmentation chain transfer polymerization (RAFT) [11]. SFRP is based on the use of nitroxide radicals such as 2,2,6,6-tetramethyl-1-piperidinyl-1-oxy

(TEMPO) as reversible terminating agent to react with the growing polymer chain. Both SFRP [12] and ATRP [13, 14] have been used to prepare graft copolymers.

This paper describes the synthesis of a high transition temperature (Tg) *N*-substituted maleimide-methylvinylisocyanate copolymer with TEMPO moiety at the side chain, and the application of this polymer as a polymeric counter radical in the radical polymerization of styrene to yield corresponding graft copolymers. Such approach has been previously applied to prepare well defined block copolymers of styrene with polytetrahydrofuran [15] and poly(ε-caprolactone) [16].

The polymers of *N*-phenylmaleimide and its derivatives have been known to exhibit high Tg due to the rigid imide rings in the backbones. The polymerization of vinyl isocyanate with maleic anhydride is known to be alternating [17] and similar tendency for the maleimide systems is also observed [18]. Therefore, a well defined copolymer with a 1:1 composition is formed from a polymerization of a 1:1 mixture of monomers and there is one reactive isocyanates group in every repeating unit of the copolymer. In a subsequent process, the polymers can be functionalized by reaction with hydroxy group of 4-hydroxy TEMPO. As it will be shown below, these polymers behave as polymeric counter radicals for propagating polymeric radicals.

## Experimental

Phenyl maleimide monomer was prepared according to the literature procedure [19]. Vinyl isocyanate was prepared via Curtius reaction from methacryloyl chloride and redistilled before use. All preparations, requiring inert media because of the isocyanates, were carried out in solvents dried by literature procedures. Styrene and solvents were purified by conventional drying and distillation procedures. 4-hydroxy-TEMPO (Aldrich) and benzoyl peroxide (BPO) were used without further purification.

### *Analysis*

$^{1}$H-NMR spectra were taken on a Bruker 250 MHz spectrometer in $CDCl_3$ solution with tetramethylsilane as the internal standard. The size exclusion chromatography (SEC) analysis were performed with a set up consisting of a Waters pump (model 600E) and three ultrastyragel columns with porosities $10^4$, 500 and 100 A°, respectively. THF was used as the eluent at a flow rate of 1 ml min$^{-1}$ and the detection was achieved with Waters differential refractometer (model 410). Molecular weights were calculated using polystyrene standards.

The UV/VIS spectra were taken on a Perkin-Elmer spectrophotometer (Lambda-2) with solvent $CH_2Cl_2$. IR spectra were measured on a Jasco FT-IR 5300.

### *Preparation of Phenylmaleimide-Methylvinylisocyanate Copolymer (PMCP) (3)*

Polymerizations were carried out in dry reaction flasks with nitrogen inlet. The comonomers, *N*-phenylmaleimide **(1)** (2g, 11,55 mmole) and methylvinylisocyanate **(2)** (1,15g, 13,86 mmole) were dissolved in dry toluene (10 % wt solution) and 2 mol % of 2,2'-azoisobutyronitrile (AIBN) were added. The mixture was degassed in a freeze-pump-thaw cycle and then polymerized at 60 °C for 17 h. Polymers were precipitated in dry diethylether, and separated by filtration and finally dried at ca. 40 °C in vacuo. Yield: 93 %.

Elemental analysis: Calcd. for $(C_{14}H_{12}N_2O_3)_n$: C:65,62; H:4,72; N:10,93; O:18,73 Found C:65,65; H:5,03; N:10,74; O:18, 58, $^1$H-NMR ($CDCl_3$): 7-7.5 ppm (m, 5H, aromatics), 1,5-3.6 ppm (s, m, $CH_3$, $CH_2$, CH, 7H, aliphatics).

### *Preparation of TEMPO-Phenylmaleimide-Methylvinylisocyanate Copolymer (TEMPOPMCP) (5)*

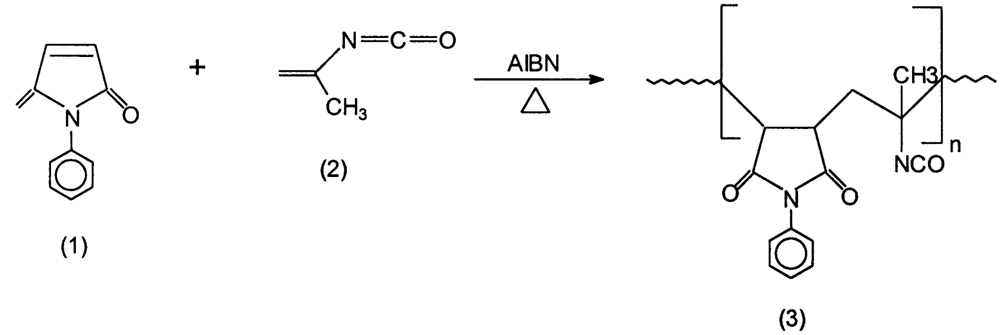
To solution of PMCP (0.3 g), in dry THF (10 ml) was added 4-hydroxy-TEMPO (2.34 mmol) and 2 mol % of dibutyl-tin-dilaurate as a catalyst. The mixture was stirred at 50 °C for 5 days under nitrogen atmosphere. Decomposition of NCO group was followed by the change in intensity of the peak at 2254 $cm^{-1}$ in the IR spectra of the polymer during the reaction. Upon dissapperance of NCO group polymers were treated with the methanol to quench remaining trace NCO groups. The solutions were then poured into diethylether, the precipitated polymers were filtered off and dried in vacuo. The polymers were purified by repeated precipitation from dichloromethane into diethylether.

### *Radical Polymerization of Styrene in the Presence of TEMPO-PMCP*

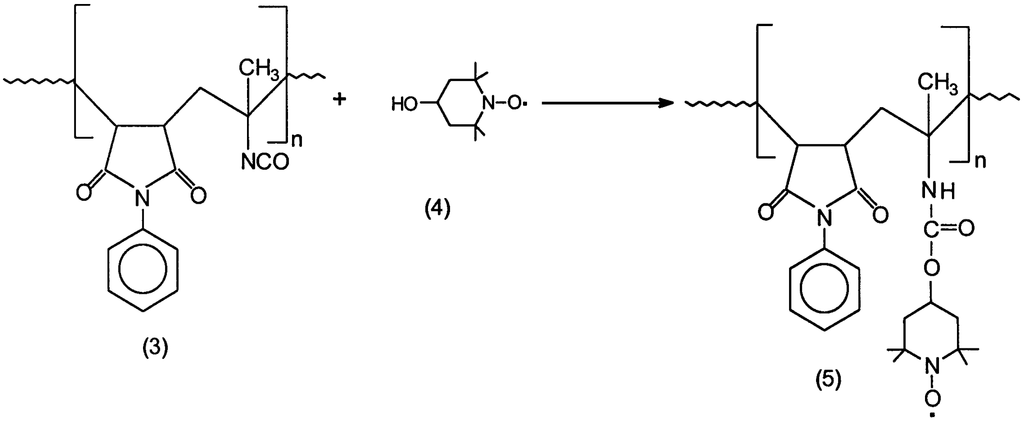
Styrene (8,73 mol), BPO (0,058 mmol) and TEMPO-PMCP (0,06 g,) in toluene were purged with nitrogene. The polymerization was carried out at first for 3,5 h at 95 °C and then continued for another 24 h at 125 °C. At the end of the reaction, polymers were precipitated into methanol and dried.

## Results and Discussion

Phenylmaleimide and methylvinylisocyanate were chosen as comonomers. Because of the prevented rotation around C-C bonds in five membered ring structure of maleimides, their polymerization give to a rigid polymer chain and high Tg values.



As a second comonomer, methylvinylisocyanate allows an easy reaction with simple OH functionalities such as 4-hydroxy TEMPO. Two fold excess of alcohol was used in the reaction since the imide ring does not react with alcohols under conventional conditions. The reaction was catalysed with dibutyltin(IV) dilaurate and prolonged reaction time was required for complete conversion of isocyanate. The remaining isocyanates have to be converted to urethanes with methanol to avoid side rections.



The IR and $^1$H-NMR spectra prove the expected structure of the polymer. The $^1$H-NMR measurement of the TEMPO incorporated product was performed in the presence of phenylhydrazine since TEMPO moiety can easily be reduced by hydrazines to the corresponding hydroxylamine. According to the $^1$H-NMR spectrum, the signals originating from TEMPO were discerned at 1.26, 1.42, 1.62 and 1.86 ppm. These signals were assigned to two types of methyl protons, axial and equatorial and two methylene ones axial and equatorial, respectively. The signal at 5.17 ppm also originates from TEMPO and assigned to the OH protons. Moreover, the prepolymer had characteristic absorption $\lambda_{max}$ at 460 nm originating from the stable nitroxyl radical.

Radical polymerization of styrene was performed with BPO as an initiator in the presence of the above obtained prepolymer (TEMPO-PMCP). Usual stable radical mediated polymerization prodecure was followed i.e., 125 °C after being held at 95 °C for 3.5 h.

The results are shown in Table 1. It is interesting to note that the polydispersities decreased as the polymerization proceeded indicating good control of the system. Figure 1 illustrates a typical SEC profile before and after free radical polymerization. The graft copolymer showed a unimodal SEC curve and shifted to higher molecular weight elution volume. Notably no peak due to the prepolymer was observed. Although the presence of polystyrene graft was evidenced by $^1$H-NMR spectra, estimation of the composition of the graft copolymers was not possible since the peaks of the aromatic protons of styrene overlap with those of the phenyl isocyanate groups.

As can be seen from Table 2, two distict glass transition temperatures representing those of the backbone and graft chains are observed indicating incompatibilty of the both segments.

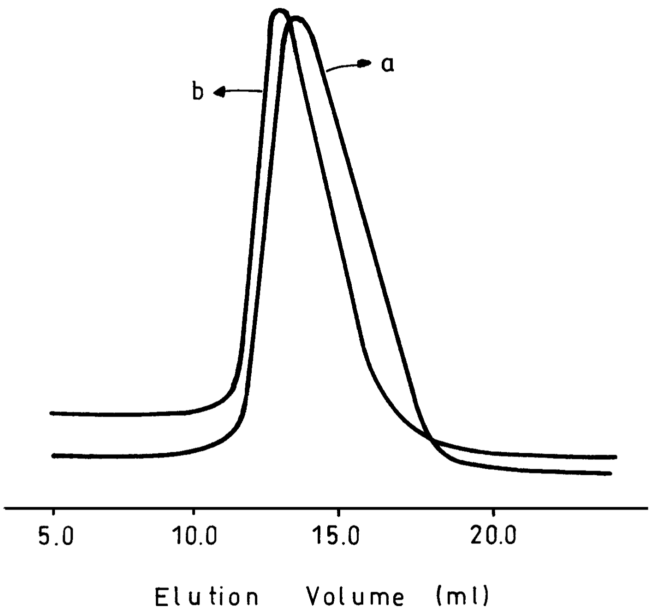


**Figure 1.** SEC traces of (a) TEMPO-PMCP (5) and (b) the graft copolymer (6b)

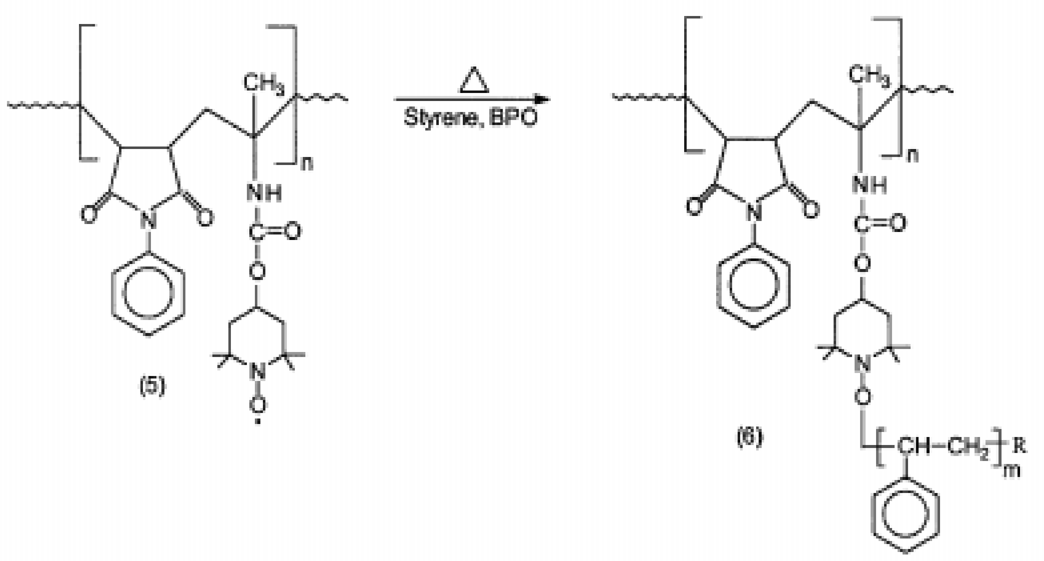


**Table 1.** Radical polymerization of styrene by BPO and TEMPO-PMCP in toluene, [BPO]=5,8.10$^{-3}$ mol l$^{-1}$

| TEMPO-PMCP[a] (g l$^{-1}$) | Monomer (mol l$^{-1}$) | Time (h) | Conversion (%) | Mn | Mw/Mn | Polymer |
|---|---|---|---|---|---|---|
| 30 | 4.4 | 20 | 26 | 34000 | 1.4 | 6a |
| 30 | 4.4 | 45 | 37 | 41100 | 1.5 | 6b |
| 30 | 2.2 | 16 | 16 | 31500 | 1.5 | 6c |

[a] Mn=28000, Mw/Mn=1.9

**Table 2.** Thermal behaviour of the polymers

| Polymer Samples[a)] | $T_g$(°C)[b)] | $T_d$(°C)[c)] |
|---|---|---|
| 1 | 202 | 280 |
| 5 | 207 | 278 |
| 6a | 103-207[d)] | 260 |
| 6b | 103-206[d)] | 258 |
| 6c | 101-205[d)] | 255 |

[a)] Refer formulas in the text for denotation

[b)] Glass transition temperatures; heating rate:10 $^0$C min$^{-1}$

[c)] Decomposition temperatures

[d)] Glass transition temperatures of polystyrene and poly(*N*-phenylmaleimide-co-vinylmethylisocyanate) segments.

In conclusion the synthesis of phenylmaleimide-methyl vinylisocyanate copolymers with nitroxy radicals at the side chains was achieved. The resulting polymers were able to serve as polymeric counter radicals in the polymerization of styrene to give the corresponding graft copolymer. Previous reports on the preparation of graft copolymers by stable free radical polymerization method involves either the use macromonomer [20] in standart nitroxide mediated radical polymerization or cleavage of dormant alkoxyamine that reversibly produces propagating radicals at the side chain [21, 22]. Our work can be regarded as the first attempt to preapare graft copolymers by polymeric counter radical approach in stable free radical polymerization.

## Acknowledgements

The authors would like to thank the I.T.U Research Fund for financial support. A graduate's fellowship from TÜBİTAK (BDP program) for A.B.D. is gratefully acknowledged.

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