

# Metal-catalyzed Living Radical Graft Copolymerization of Styrene Initiated from Arylated Poly(vinyl chloride)

Mojtaba Abbasian and Ali Akbar Entezami\*

Laboratory of Polymer, Faculty of Chemistry, University of Tabriz,  
Tabriz-5166414776, Iran

Received 21 December 2005; accepted 14 March 2006

## ABSTRACT

PVC is one of the world's major polymers and a large amount of PVC is produced worldwide for its superior mechanical and physical properties. Graft copolymerization of PVC with monomers such as styrene has been examined to improve the thermal stability of PVC. This graft copolymerization was carried out by atom transfer radical polymerization (ATRP). In this method PVC was condensed with toluene in mild condition (toluene as arylating agent,  $\text{AlCl}_3$  complexed with nitrobenzene as catalyst and THF as diluent) and we used arylated PVC (PVC-ph) as a starting polymer and *N*-bromosuccinimide as a brominating agent to obtain polymers with bromine group. This brominated PVC was used as a macroinitiator. This macroinitiator can polymerize styrene in the presence of  $\text{CuCl}/\text{bpy}$  catalyst system in THF solvent at  $90^\circ\text{C}$ . The formation of the graft copolymer was confirmed with GPC, DSC,  $^1\text{H}$  NMR and FTIR spectroscopy. This approach using a macroinitiator is an effective method for the preparation of new materials.

### Key Words:

living radical polymerization;  
polystyrene;  
poly(vinyl chloride);  
arylation;  
atom transfer radical polymerization;  
graft copolymerization.

## INTRODUCTION

Poly(vinyl chloride) (PVC) is a major commercial polymer [1]. Over 20 million metric tons of PVC per year are currently produced worldwide. PVC is light, flame-retardant, robust and durable; it has low permeability to gases and good

weatherability and its physical and mechanical characteristics make it ideal for many different uses. PVC is well known for its compatibility with additives including plasticizers, heat stabilizers, lubricants, fillers, and other polymers which

(\*) To whom correspondence to be addressed.

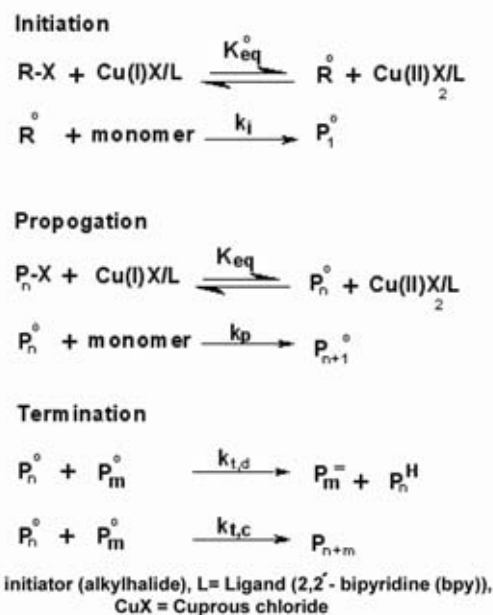
E-mail: [entezami@tabrizu.ac.ir](mailto:entezami@tabrizu.ac.ir)

enable it to have a variety of mechanical properties. However, fluid plasticity and thermal stability of PVC are inferior to these of other commodity plastics such as polyethylene and polystyrene. Chemical modification of PVC has also been of interest. One way to achieve this goal is by grafting onto PVC [2]. Several reports have appeared on the subject of the grafting of monomers onto PVC [3]. Anionic [4] and radical [5] processes have been applied to prepare graft copolymers with PVC as a backbone.

The rapidly developing field of controlled radical polymerization provides another approach to prepare graft copolymers, especially with well-defined structures. In controlled radical polymerization, the concentration of growing radicals is suppressed to avoid termination. This is made possible by using various means such as iniferters, 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) [6,7], organometallic species [8], degenerative transfer and atom transfer [9].

One of the representative accomplishments obtained in the area of living radical polymerization should be atom transfer radical polymerization invented by both Matyjaszewski and Sawamoto in 1995 [8,10]. Atom transfer radical polymerization is a living radical polymerization system that has been demonstrated to successfully polymerize a series of vinyl monomers such as styrene as well as its derivative, (meth)acrylate and acrylonitrile [11]. It is proved that the application of ATRP has resulted in the synthesis of polymers with very narrow molecular weight distribution  $M_w/M_n < 1.1$ . Irrespective of the number and type of monomer, which can be successfully polymerized by atom transfer radical polymerization (ATRP) has also been shown to be more versatile with respect to the novel polymer architectures such as graft copolymer, block copolymer, and (hyper) branched polymers [12]. Inherent in the mechanism of ATRP is the incorporation of the halogen at the chain ends. The alkyl halide end groups can be transformed into other functionalities through standard organic procedures, which involve azide and amino groups [13], hydroxyl end groups [14], acetate and phosphonium end groups [15], and allyl end groups [16]. Monomers such as allyl alcohol, 1,2-epoxy-5-hexene, silyl enol ether and bicyclic olefin were also used to modify the halogen end groups [17].

ATRP employs equilibrium between dormant



**Scheme I.** Mechanism of ATRP.

alkyl halides and active propagating radicals to maintain a low concentration of active species. The activated radical species can either propagate or be deactivated to reform the dormant species (Scheme I). ATRP also has an advantage in utilizing a wide range of initiators. Alkyl halides with radical stabilizing substituents such as carbonyl, cyano, or aryl groups adjacent to the C-X, can be used as initiators. In addition to compounds containing activated carbon-halogen bonds, those compounds with weak halogen bonds, like  $\text{RSO}_2\text{-X}$  [18] are good initiators. Any compound, including macromolecular species, can potentially be used to initiate ATRP as long as they contain activated halogen atoms.

In this work we present the preparation of grafted PVC with styrene using a macroinitiator brominated of arylated PVC (PVC-ph-Br). The incorporated bromine groups were utilized as initiator for ATRP. The PVC backbone remained intact during ATRP because the chlorine on the PVC backbone is very strongly bonded to initiate the polymerization.

## EXPERIMENTAL

### Materials

Poly(vinyl chloride) was provided by Fluka. Styrene (Tabriz Petrochemical Co.) was distilled under

reduced pressure. Toluene, THF, chloroform were dried by refluxing over sodium and distilled under argon prior to use.

2,2'-Bipyridine (bpy) and 2,2'-azobisisobutyronitrile (AIBN), were used without purification. Cuprous chloride and *N*-bromosuccinimide (NBS) were purchased from Merck and purified and dried by conventional methods before using [19]. All other chemicals were purchased from Merck and used without further purification. Aluminium trichloride was purchased from Aldrich.

### Instrumentation

<sup>1</sup>H NMR Spectra were recorded on FT NMR (400 MHz) Bruker in CDCl<sub>3</sub>. FTIR Spectra were recorded using Shimadzu FTIR-8101 M. The molecular weight of the resulting polymers was obtained with a maxima 820 GPC analysis instrument using polystyrene (10<sup>6</sup>, 10<sup>5</sup>, 10<sup>4</sup> A<sup>0</sup>) calibration standards with a tetrahydrofuran (THF) mobile phase.

Differential scanning calorimetry (DSC) analyses were performed on a Mettler 4000 TA thermal analytical system.

### Condensation of PVC with Toluene

The Friedel-Crafts reactions were carried out in ground-glass stoppered flasks fitted with dropping funnel and a reflux condenser. A THF solution (20 mL) of poly(vinyl chloride) (PVC) (1 g) was added under argon to a stirred solution of toluene (2 mL, 0.018 mol), AlCl<sub>3</sub> (1 mol) in nitrobenzene (12.5 mL). The mixture was stirred for 24 h at room temperature and then precipitated into acidified 80% methanol (v/v 1000 mL; 15 mL of HCl). The resulting product was dissolved in THF, then reprecipitated into 80% methanol and washed with methanol then dried at 40°C under vacuum. Yield: 1.5 g (white powder). FTIR (KBr, cm<sup>-1</sup>): 3075 (phenyl protons of toluene) 1608 (-C=C- protons of phenyl groups) 1476 (-CH<sub>3</sub> protons of toluene groups). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ=7.55-7.70 (phenyl protons of toluene), δ=2.00-2.36 (-CH<sub>3</sub> protons of toluene groups), δ= 4.27- 4.58 (-CH protons of PVC).

### Bromination of Arylated PVC

*N*-Bromosuccinimide (NBS, 0.2 g) and AIBN (0.03 g) were added to a suspension of arylated PVC (1 g) in

CCl<sub>4</sub> (40 mL) in a 250 mL round bottomed flask with a magnetic stirring bar. After refluxing at 90°C for 5 h, the reaction mixture was filtered and washed well with acetone and then dried overnight under vacuum for 24 h. Yield: 1.09 g. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ= 7.55-7.70 (phenyl protons of toluene), δ=2.00-2.36 (-CH<sub>3</sub> protons of toluene groups), δ = 4.27-4.58 (-CHCl protons of PVC and CHBr protons of brominated of arylated PVC).

### Synthesis of PVC-g-PS by ATRP

The ATRP copolymerization was carried out under nitrogen in a dried schlenk flask equipped with a magnetic stirring bar. The flask was charged with brominated of arylated PVC (PVC-ph-Br) (0.2 g) and 5 mL of dried THF. After complete dissolution under stirring, CuCl (0.015 g, 0.158 mmol) and bpy (0.07 g, 0.47 mmol) were added. The system was degassed to remove oxygen by stirring the solution under nitrogen for 1 h. Then styrene (10 mL, 0.87 mol) was added and the flask was immersed in an oil bath and stirring was continued at 90°C for 4 h. The mixture was precipitated into methanol and obtained powder was dried at room temperature under vacuum, then the obtained powder was extracted by refluxing in cyclohexane during overnight, in order to remove PS homopolymer.

Yield: 0.3 g, <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 1.22-2.36 (-CH<sub>3</sub> protons of toluene and -CH<sub>2</sub> protons of PVC), δ=4.27-4.58 (-CH protons of PVC), 6.39-7.43 (phenyl protons of toluene).

## RESULTS AND DISCUSSION

### Acylation Reaction

Friedel-Crafts acylation reactions are aromatic substitution reactions in which benzene (or substituted benzene) undergoes acylation when treated with carboxylic acid derivatives (usually acyl halide or anhydride) and a Lewis acid catalyst (such as AlCl<sub>3</sub>) [20]. However, the Lewis acid catalyst used in these reactions may lead to chain scission, and thus changes the molecular mass of the polymers, under certain conditions. In many instances, especially in the functionalization of cross-linked polystyrene, chain cleavage is of little significance. However, even a relatively small

extent of chain scission leads to a significant broadening of the molecular-mass distribution of monodisperse polymer. Thus, reaction conditions must be mild enough to avoid any chain scission in the preparation of monodisperse carboxylated and arylated polymers [21]. In order to overcome this problem, Hird and Eisenberg [22] reported a simple method for the preparation of partial *p*-carboxylation of linear polystyrene and other polymers without degradation or cross-linking of the polymer. It is well established that, in Friedel-Crafts acylation reaction, when aluminium chloride and acetyl chloride or aryl group are allowed to react together prior to addition to the substrate, the ratio of catalyst to acyl or aryl remains con-

stant throughout the reaction, and the results are reproducible.

Another method using a mild catalyst and reaction conditions ( $\text{AlCl}_3$  complexed with nitrobenzene as a homogeneous catalyst) to overcome this problem [11,23]. According to this method, we used toluene as arylating agent,  $\text{AlCl}_3$  complexed with nitrobenzene as catalyst and THF as diluent (Scheme II) [24]. The catalyst and arylation agent were allowed to react prior to addition of the substrate (PVC), according to the Perrier procedure [25].

We characterized the resulting arylated poly(vinyl chloride) (PVC-ph) by GPC, FTIR and  $^1\text{H}$  NMR spectroscopy. FTIR Spectra for the arylated PVC is

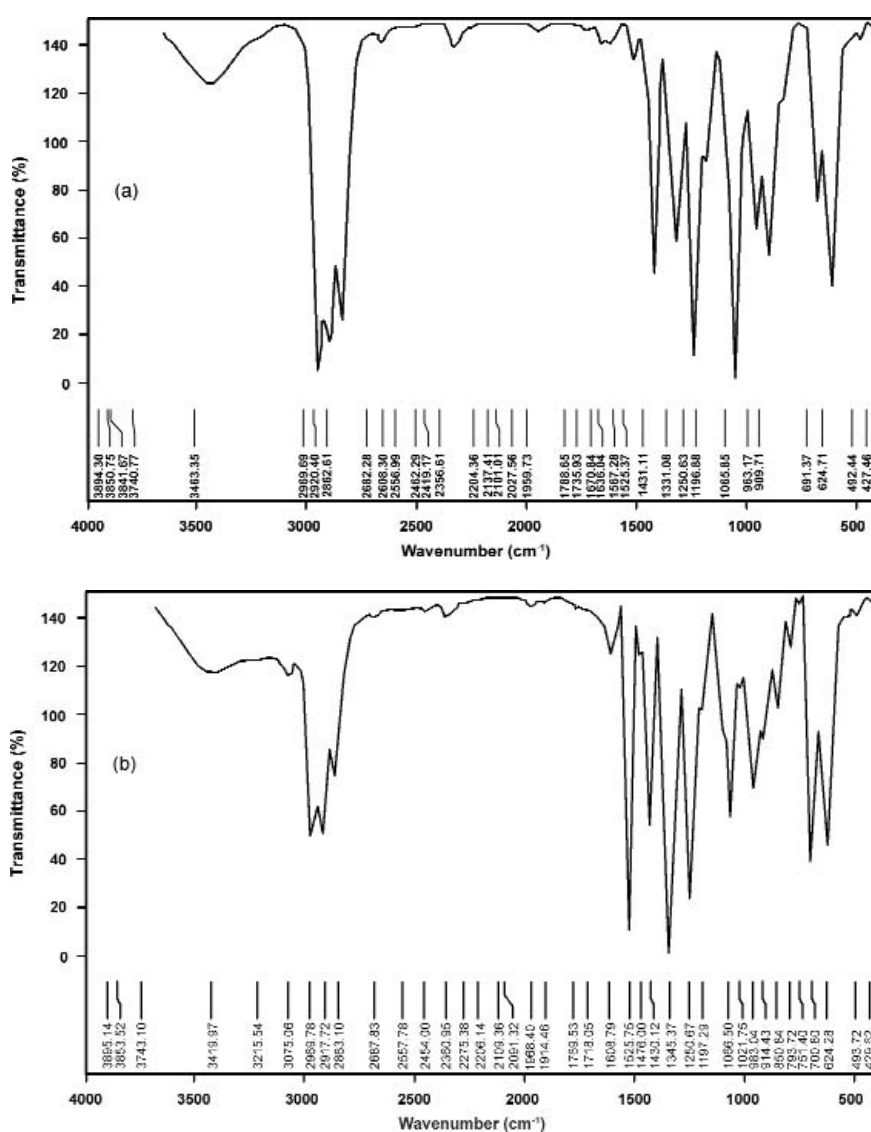
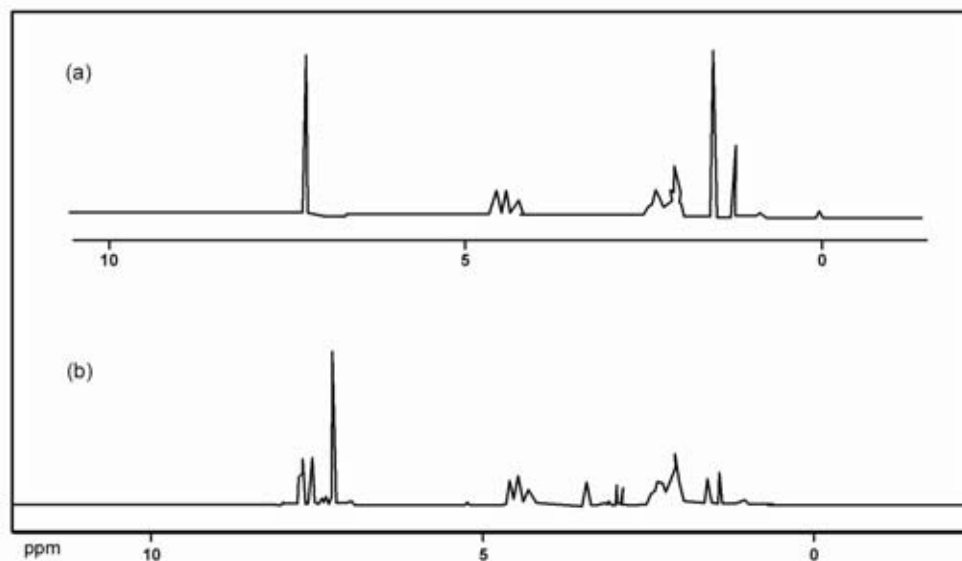


Figure 1. FTIR Spectra of poly(vinyl chloride) (A) and arylated poly(vinyl chloride) (B).



**Figure 2.** <sup>1</sup>H NMR Spectra of poly(vinyl chloride) (A) and arylated poly(vinyl chloride) (B).

shown in Figure 1.

FTIR Spectra of arylated PVC exhibits an absorption band at  $1476\text{ cm}^{-1}$  attributed to methyl stretching bond of toluene and absorption band at  $3075\text{ cm}^{-1}$  and  $1608\text{ cm}^{-1}$  attributed to aromatic stretching bond.

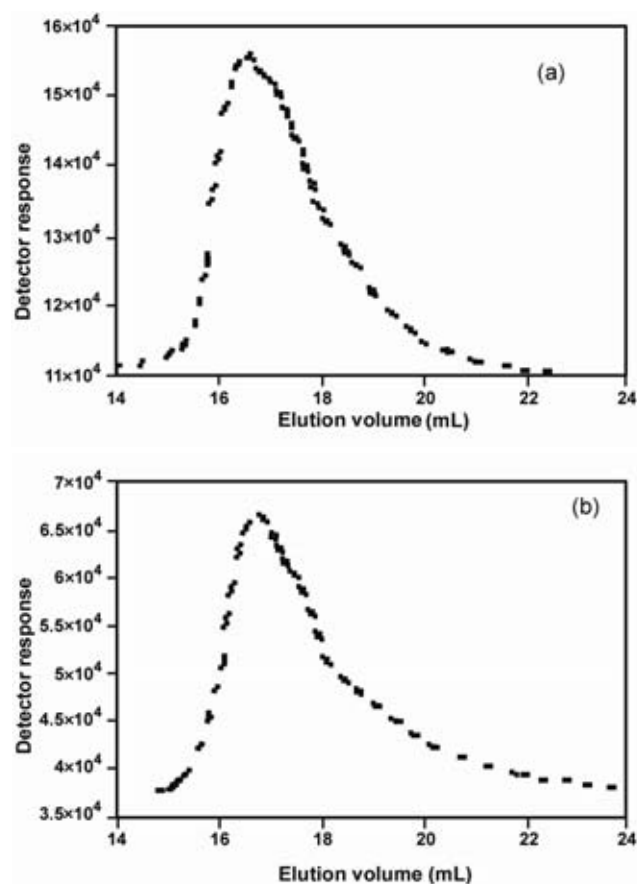
Figure 2a,b shows the <sup>1</sup>H NMR spectra of obtained arylated PVC from Friedel-Crafts arylation of PVC. It is obvious that the peak at  $\delta=7.55\text{-}7.70\text{ ppm}$  could be attributed to aromatic protons, and aliphatic protons of toluene group could be attributed to the peak at  $2.00\text{-}2.36\text{ ppm}$ , respectively.

The GPC trace of the PVC and arylated PVC (Figure 3a,b) was unimodal and showed no tailing or broadening of molecular-weight distribution, thus confirming that no cross-linking or chain scission occurred during the functionalization procedures [23].

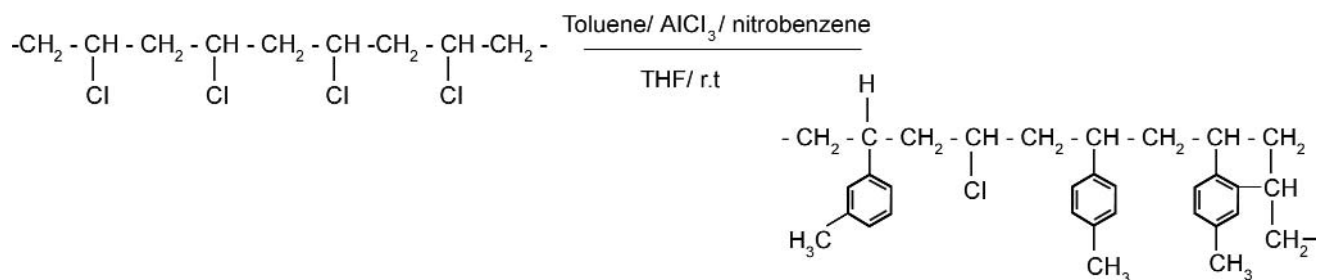
### Bromination of Arylated PVC

We used arylated PVC (PVC-ph) as a starting polymer and *N*-bromosuccinimide as a brominating agent to obtain polymers with bromine group (Scheme III). *N*-Bromosuccinimide is usually used [32] for the introduction of bromine to allylic or benzylic position. Thus, both methyl groups and backbone methine carbons can be brominated in PVC-ph. <sup>1</sup>H NMR Spectrum of synthesized brominated PVC-ph confirms bromination of methyl and methine groups. However, due to signal position of peaks in <sup>1</sup>H NMR

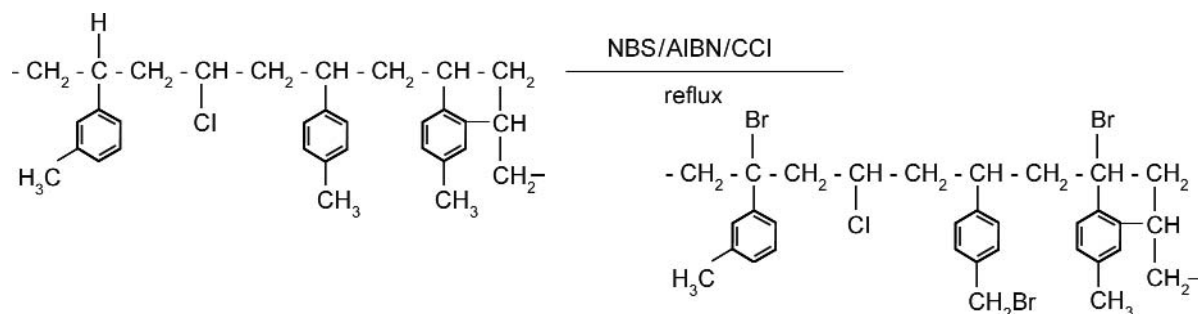
spectroscopy, because the chemical shift of CH-Br



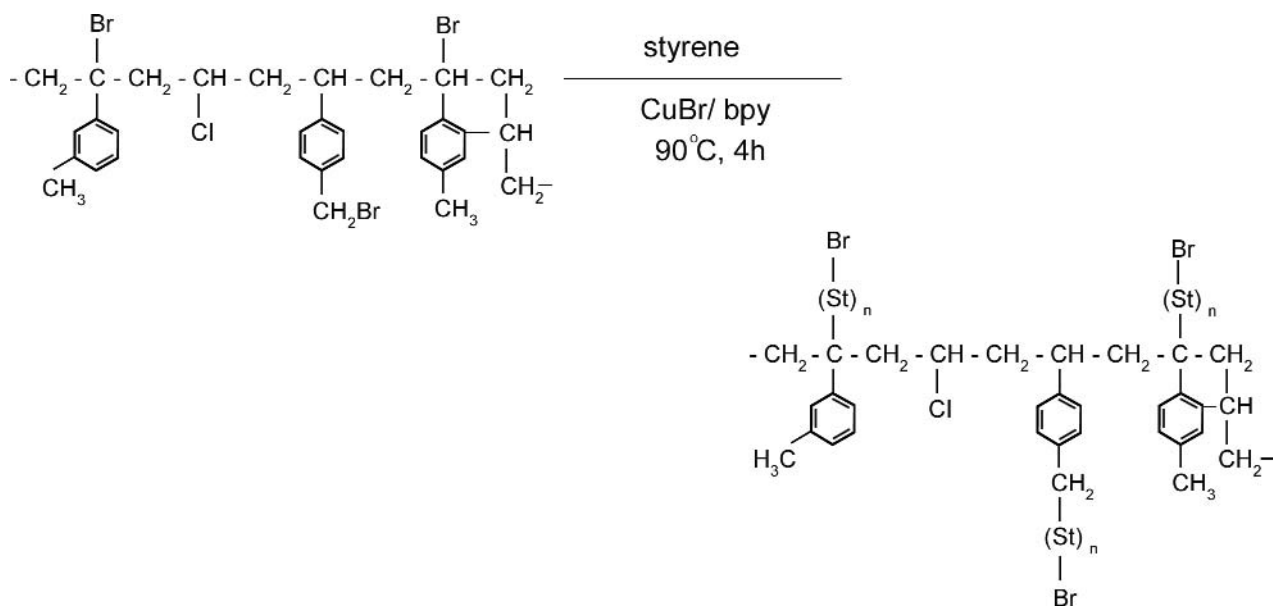
**Figure 3.** GPC Trace of poly(vinyl chloride) (a) and PVC-ph-Br (b).



Scheme II. Arylation of poly(vinyl chloride).



Scheme III. Bromination of arylated poly(vinyl chloride).



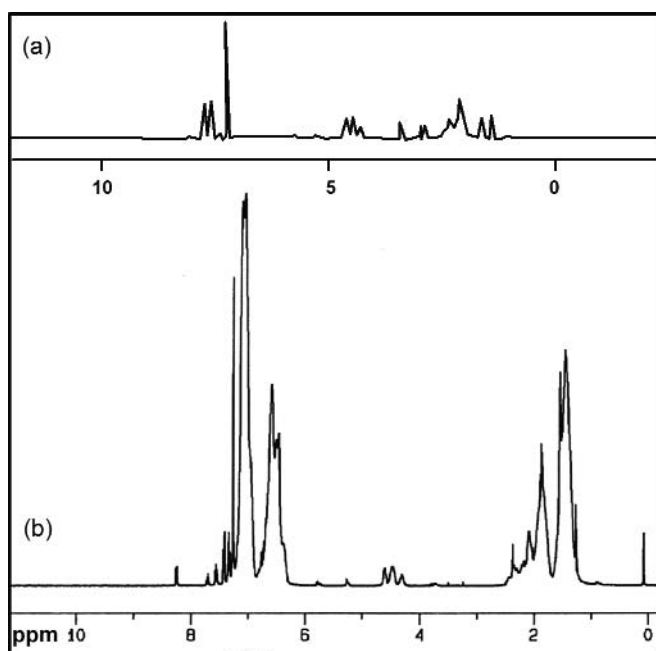
Scheme IV. Graft copolymerization of PS onto poly(vinyl chloride).

and CH-Cl are similar, therefore, does not change in the chemical shift of CH-Cl whereas decreases the integration intensity of aliphatic hydrogens.

### Graft Copolymers

The synthesis of graft copolymers can be accom-

plished through one of the three following routes: (I) "grafting from" reactions (utilizing polymerization of grafts from a macroinitiator with pendant functionality), (II) "grafting through" processes (operating by homo- or copolymerization of a macromonomer) and (III) "grafting onto" (occurring when the growing



**Figure 4.** <sup>1</sup>H NMR Spectroscopy of PVC-ph-Br (A) PVC-g-PS (B).

chain is attached to a polymer backbone). The first two methods have been used in conjunction with ATRP in the design of graft copolymers and underscore the versatility of this controlled radical polymerization technique to synthesize a variety of (co)polymers [26].

#### Synthesis and Characterization of PVC-g-PS

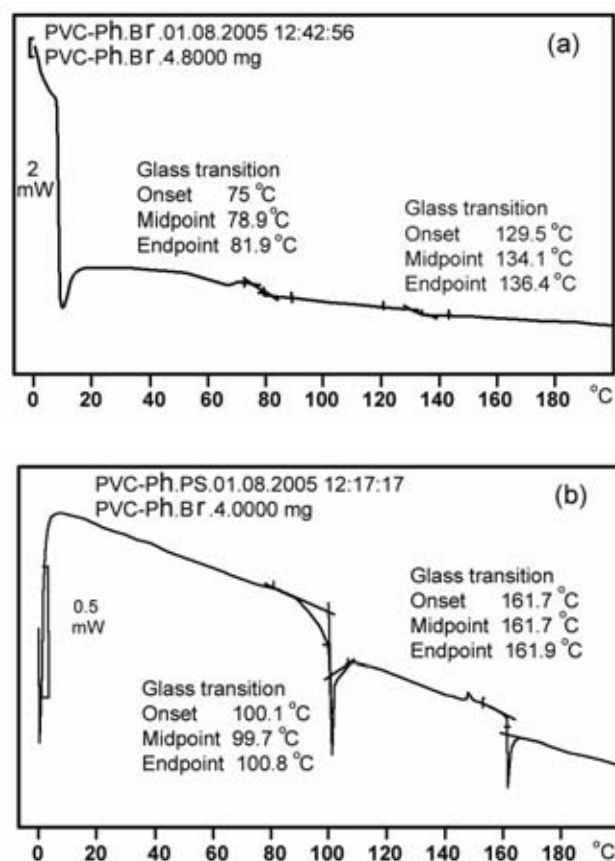
The graft copolymerization of styrene initiated by the PVC-ph-Br as macroinitiator in the presence of CuCl/bpy catalyst system was first studied in THF solvent to solubilize the catalyst and also the arylated poly(vinyl chloride) at 90°C (Scheme IV). The graft copolymer was analyzed by <sup>1</sup>H NMR spectroscopy (Figure 4).

The <sup>1</sup>H NMR of the purified product (Figure 4) indicates the formation of graft copolymer PVC-g-PS, since with comparison intensity of the peaks at 6.49-6.75 ppm and 7.03-7.41 ppm with arylated PVC determine that styrene repeat unit was incorporated onto PVC backbone.

The mechanism of graft copolymerization of styrene onto PVC by ATRP is presumably similar to that proposed for the ATRP with other vinyl monomers such as (meth)acrylates and acrylonitrile [9,27] (Scheme IV).

Additional evidence on the effectiveness of the graft copolymerization was also obtained from DSC

data. The graft copolymer studied in this work consists of poly(vinyl chloride) backbone carrying poly-



**Figure 5.** DSC Thermogram of PVC-ph-Br (A) and PVC-g-PS (B).

styrene. Two  $T_g$ 's were observed in the purified product of PVC-g-PS, one at 99.8°C and the other at 161.8°C. This demonstrates the presence of microphase separation in this graft copolymer. This was an expected result because it is well known that polystyrene is immiscible with PVC [28,29] (Figure 5a,b).

The GPC trace of the grafted copolymer (Figure 6a,b) was bimodal and showed the incompleting initiation of the graft copolymer of styrene by PVC-ph-Br macroinitiator [30]. Furthermore, the polymer peak continuously shifted to higher molecular weights with monomer conversion. The molecular weight of the macroinitiator was  $M_n = 16179$ ,  $M_w/M_n = 4.39$ . After 10 h polymerization the measured values had increased to  $M_n = 251360$ ,  $M_w/M_n = 2.22$ .

The polydispersity decreased with the progress of the polymerization demonstrating that the reaction was controlled and the polystyrene grafts had low polydispersities typical of radical polymerization by atom transfer process [31].

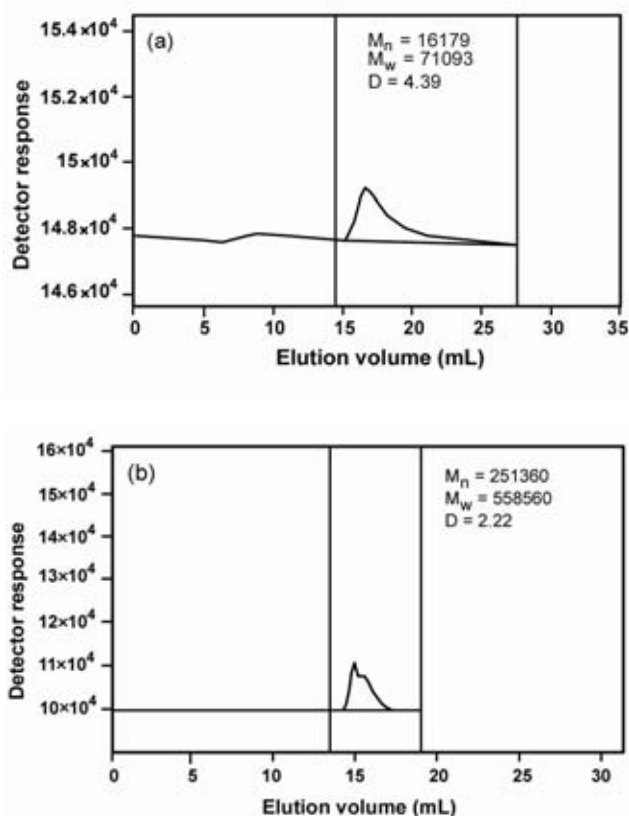


Figure 6. GPC Trace of PVC-ph-Br (A) and PVC-g-PS (B).

## CONCLUSION

The graft copolymers composed of poly(vinyl chloride) as a backbone and polystyrene as branches were obtained for the first time by atom transfer radical polymerization (ATRP) techniques. New reaction condition using mild state is employed to synthesize controlled graft copolymers. These reaction conditions can overcome the problem of gelatin and cross-linking in the synthesis of similar graft copolymers reported in the literature. The formation of the graft copolymer was supported by analysis of GPC, DSC, <sup>1</sup>H NMR and FTIR spectroscopy.

## ACKNOWLEDGEMENTS

The authors express their gratitude to the Iran Polymer and Petrochemical Institute for providing facilities to scan GPC of polymer samples.

## Abbreviations

ATRP: Atom transfer radical polymerization  
 Bpy: 2,2' Bipyridine  
 CuCl: Copper chloride  
 THF: Tetrahydrofuran  
 TEMPO: 2,2,6,6-Tetramethyl-1-piperidinyloxy  
 GPC: Gel permeation chromatography  
 DSC: Differential scanning calorimetry  
 Br: Bromine  
 THF: Tetrahydrofuran  
 AIBN: 2,2'-Azobisisobutyronitrile

## REFERENCES

- Smallwood P.V.S., Vinyl Chloride Polymers, Polymerization, in: *Encyclopedia Polym. Sci. Eng.*, **17**, 2nd ed, Mark H.F., Bikales N.M., Overberger C.G., Menges G., Kroschwitz J.I. (Eds.), Wiley, New York, 295, 1985.
- Remp P.F., Lutz P.J., Synthesis of graft copolymers, in: *Comprehensive Polym. Sci.*, **6**, Eastmond G.C., Ledwith A., Russo S., Sigwalt P. (Eds.), Pergamon, Oxford, 403, 1989.
- Kiyoshi E., Synthesis and structure of poly(vinyl chloride), *Prog. Polym. Sci.*, **27**, 2021-2054, 2002.



- Kucera M., Salajka Z., Majerova K., Reactions of macroions leading to graft copolymers: Crosslinking and grafting of PVC by carbanions, *Polymer*, **26**, 1575-1581, 1985.
- Hegazi El.A., E vaid A.R., Sharabasy S.A.El., Mousa A.M., Hassan A.Y., Radiation grafting of MMA onto PVC films, *J. Appl. Polym. Sci.*, **41**, 2941-2950, 1990.
- Abbasian M., Namazi H., Entezami A., Living radical graft polymerization of styrene to styrene butadiene rubber (SBR) with 2,2,6,6-tetramethyl-1-piperidinolxy (TEMPO), *Polym. Adv. Technol.*, **15**, 606-611, 2004.
- Bani F., Abbasian M., Afshar Taromi F., Entezami A., Polystyrene grafted to ABS backbone by living radical polymerization with TEMPO, *Iran. Polym. J.*, **13**, 513-520, 2004.
- Wang J.S., Matyjaszewski K., Controlled/living radical polymerization. Atom transfer radical polymerization in the presence of transition-metal complexes, *J. Am. Chem. Soc.*, **117**, 5614-5615, 1995.
- Alipour M., Massoumi B., Dindar Safa K., Entezami A., Living radical polymerization of methyl methacrylate, methyl acrylate and their block copolymers with acrylonitrile by atom transfer radical polymerization, *Iran. Polym. J.*, **10**, 99-106, 2001.
- Kato M., Kamaigaito M., Sawamoto M., Higashimura T., Polymerization of methyl methacrylate with the carbon tetrachloride/dichlorotris-(triphenyl phosphine) ruthenium (II)/methyl aluminium bis(2,6-di-ter-butyl phenoxide) initiating system: Possibility of living radical polymerization, *Macromolecules*, **28**, 1721-1723, 1995.
- Tizpar S., Abbasian M., Afshar Taromi F., Entezami A., Grafting of polymethylmethacrylate and polyacrylonitrile onto polystyrene using atom transfer radical polymerization technique, *J. Appl. Polym. Sci.*, in press, 2006.
- Wang G., Shi Y., Fu Z., Yang W., Huang Q., Zhang Y., Controlled synthesis of poly( $\epsilon$ -caprolactone)-*g*-polystyrene by atom transfer radical polymerization with poly( $\epsilon$ -caprolactone-*co*-*a*-bromo- $\epsilon$ -caprolactone) copolymer as a macroinitiator, *Polymer*, **76**, 10601-10606, 2004.
- Coessens V., Matyjaszewski K., Synthesis of polymers with amine end groups by atom transfer radical polymerization, *J. Macromol. Sci. Pure Appl. Chem.*, **36**, 811-826, 1999.
- Coessen V., Matyjaszewski K., Synthesis of polymers with hydroxyl end groups by atom transfer radical polymerization, *Macromol. Rapid Commun.*, **20**, 127-134, 1999.
- Coessens V., Matyjaszewski K., Synthesis of polymers with phosphonium end groups by atom transfer radical polymerization, *J. Macromol. Sci. Pure Appl. Chem.*, **36**, 653-666, 1999.
- Bon S.A.F., Steward A.G., Haddleton D.M., Modification of the  $\omega$ -bromo end group of poly(methacrylate)s prepared by copper (I)-mediated living radical polymerization, *J. Polym. Sci. Part A: Polym. Chem.*, **38**, 2678-2686, 2000.
- Coessen V., Pyum J., Miller P.J., Gaynor S.G., Matyjaszewski K., Functionalization of polymers prepared by ATRP using radical addition reaction, *Macromol. Rapid Commun.*, **21**, 103-109, 2000.
- Percec V., Barboiu B., Living radical polymerization of styrene initiated by arenesulfonyl chloride and CuI (bpy)<sub>n</sub> Cl, *Macromolecules*, **28**, 7970-7972, 1995.
- Perrin D.O., Armarego W.L.F., *Purification of Laboratory Chemicals*, 3rd Ed, Pergamon, 1988.
- Andrew S.J., *Introduction to Organic Chemistry*, New York, Wiley, 1971.
- Sun G., Chen T.Y., Worely S.D., A novel biocidal styrene triazinedione polymer, *Polymer*, **37**, 3753-3756, 1996.
- Hird B., Eisenberg A., *p*-Carboxylation of linear high molecular-mass polystyrene, *J. Polym. Sci. Part A: Polym. Chem.*, **31**, 1377-1381, 1993.
- Janata M., Masar B., Toman L., Vlcek P., Policka P., Brus J., Holler P., Multifunctional ATRP macroinitiator for the synthesis of graft copolymer, *React. Funct. Polym.*, **50**, 67-75, 2001.
- Teyssie P.H., Smets G., Polymers and group interactions: II, Friedel-Crafts reaction on polyvinyl chloride, a route to poly-1,3-methyleneindans., *J. Polym. Sci.*, **20**, 351-369, 1956.
- Gore P.H., Friedel-Crafts and related reaction, 3, Part 1, Olah G.A. (Ed.), Wiley, Chichester, 1964.
- Janata M., Masar B., Toman L., Vlcek P., Latalova P., Brus J., Holler P., Synthesis of novel types of

- graft copolymer by a "grafting-form" method using ring-opening polymerization of lactones and lactides, *React. Funct. Polym.*, **57**, 137-146, 2003.
27. Matyjaszewski K., Patten T.E., Xia J., Controlled/living radical polymerization, kinetics of the homogeneous atom transfer radical polymerization of styrene, *J. Am. Chem. Soc.*, **119**, 674-680, 1997.
  28. Grulke E.A., *In: Polymer Handbook*, 3rd ed., Brandrup J., Immergut E.H. (Eds.), Wiley InterScience, New York, **VI**, 209-277, 1989.
  29. Percec V., Asgarzadeh F., Metal-catalysed living radical graft copolymerization of olefines initiated from the structural defects of poly(vinyl chloride), *J. Polym. Sci. Part A: Polym. Chem.*, **39**, 1120-1135, 2001.
  30. Shipp D.A., Wang J.L., Matyjaszewski K., Synthesis of acrylate and methacrylate block copolymer using atom transfer radical polymerization, *Macromolecules*, **31**, 8005-8008, 1998.
  31. Nakagawa Y., Miller P.J., Matyjaszewski K., Development of novel attachable and graft copolymers from poly(dimethylsiloxane) macroinitiators, *Polymer*, **39**, 5163-5170, 1998.
  32. Pizey J.S. (Ed.), *Synthesis Reagents*, 2, Ellis Horwood, Chichester, 1974.