Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

A Grafting Study on Partially Dehydrochlorinated Poly(vinyl chloride) by Atom Transfer Radical Polymerization

Mehmet Coşkun[a]; Gamze Barim[a]; Kadr Demrell[a]
[a] Faculty of Science and Arts, Department of Chemistry, University of Fırat, Elazığ-Turkey

To cite this Article Coşkun, Mehmet , Barim, Gamze and Demrell, Kadr(2007) 'A Grafting Study on Partially Dehydrochlorinated Poly(vinyl chloride) by Atom Transfer Radical Polymerization', Journal of Macromolecular Science, Part A, 44: 5, 475 — 481

To link to this Article: DOI: 10.1080/10601320701229068

URL: http://dx.doi.org/10.1080/10601320701229068

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2007) **44**, 475–481
Copyright © Taylor & Francis Group, LLC
ISSN: 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320701229068

A Grafting Study on Partially Dehydrochlorinated Poly(vinyl chloride) by Atom Transfer Radical Polymerization

MEHMET COŞKUN, GAMZE BARIM, and KADİR DEMİRELLİ
Faculty of Science and Arts, Department of Chemistry, University of Fırat, Elazığ-Turkey

Received and accepted October, 2006

HCl elimination in low ratio was first carried out from poly(vinyl chloride) to increase allylic chlorines. Partially dehydrochlorinated poly(vinyl chloride), having a macroinitiator effect, was grafted with *tert*-butyl methacrylate via atom transfer radical polymerization in the presence of CuBr/2,2′-bipyridine at 64°C in tetrahydrofuran. Original poly(vinyl chloride) was also grafted with *tert*-butyl methacrylate under the same conditions to compare with that of partially dehydrochlorinated poly(vinyl chloride). The graft copolymers were characterized by elemental analysis, FTIR, ^{1}H and ^{13}C-NMR, differential scanning calorimetry, and gel permeation chromatography (GPC). Thermal stabilities of the graft copolymers were investigated by thermogravimetric analysis as compared with those of the macroinitiators.

Keywords: PVC; graft copolymer; atom transfer radical polymerization; thermal properties

1 Introduction

Poly(vinyl chloride), PVC, is now one of the world's major polymers in view of the large production amount and having a very diversified area of usage. Several synthetic methods for grafting of PVC have been reported by radical chain transfer reaction, such as in grafting of PVC with glycidyl methacrylate (1), methyl methacrylate (2) and butyl acrylate (3), by ionic polymerization from labile chlorine in PVC, such as in the grafting with isobutylene (4, 5), with the aid of a polyperoxy radical (6), by mechanochemical reaction, such as in the grafting with vinyl alcohol (7), and by the aid of a polymer radical produced by γ-irradiation, such as in the grafting with styrene (8), methyl methacrylate (9), acrylic acide (10), and acrylamide (11). The synthesis of an amphiphilic graft copolymer composed of PVC backbone and poly(ethylene oxide) side chain from the reaction of the chlorine in PVC and the sodium salt of poly(ethylene glycol) has been reported (12). In some works, grafting of PVC was carried out in two steps (13–17). The first step contained the reaction of the chlorine atoms in PVC with some thio compounds to form a macroinitiator. In the second step, UV light decomposed the macroinitiator to macroradicals and they can further react with various monomers to form graft copolymers. An oxygen stream was also used to form macroradicals from a macroinitiator with thio side chain (18). In another work, grafting of dehydrochlorinated PVC in solution with styrene, in the presence of AIBN, was reported (19).

Metal-catalyzed living radical polymerization, also called atom transfer radical polymerization (ATRP), recently provides another approach to the preparation of graft copolymers. Polymeric species containing activated halogen atoms can potentially be used to initiate ATRP, and if this procedure was performed in the presence of a monomer, this causes the grafting of the monomer on the polymer. Grafting of styrene and various acrylates was achieved by ATRP with the chloroacetyl group being introduced to the polymer as initiating sites (20). PVC is mainly produced by radical polymerization. Radical polymerization of vinyl chloride, however, results in the formation of molecules with a number of isomeric forms and structural defects (21–23). Recently, Percec and coworkers (24, 25), and Bicak and Özlem (26) reported the utility of ATRP in the grafting of some vinyl monomers by initiation via the labile chlorines of PVC. Very recently, Chen and coworkers reported grafting of poly(vinyl chloride-*co*-vinyl acetate) with methyl methacrylate over the labile chlorines by ATRP (27).

In this study, we have reported the utility of ATRP in grafting of *tert*-butyl methacrylate(*t*BMA) via the allylic chlorines in partially dehydrochlorinated PVC (DhPVC), and the characterization of poly(vinyl chloride)-*g*-poly(*tert*-butyl methacrylate), PVC-*g*-P*t*BMA, by elemental analysis, FTIR, NMR, GPC and thermal analysis.

Address correspondence to: Mehmet Coşkun, Department of Chemistry, Faculty of Science and Arts, University of Fırat, 23119 Elazığ-Turkey. Fax: +90-0424-2330062; E-mail: mcoskun@firat.edu.tr

2 Experimental

2.1 Materials

*t*BMA (Fluka) was purified by distillation. Tetrahydrofuran (THF), methanol, 1,3-dichlorobenzene, CuBr, 2,2′-bipyridine (bpy) and piperidine (Aldrich) were used as received. PVC was obtained from a local company named Keban Plastic Co. Sodium n-butoxide was prepared by reaction of anhydrous n-butanol with metallic sodium in dry diethyl ether at room temperature.

2.2 Partially Dehydrochlorination of PVC and Grafting Procedure

According to the procedure adopted from the literature (19), partially DhPVC was prepared by HCl elimination of PVC in THF solution with piperidine (1.4 molar ratio of VC in PVC/piperidine) as a base at the reflux temperature (64°C) under argon atmosphere for 180 min, The colorless reaction solution first changed to yellow, brown and dark brown as the reaction proceeds. At the end of the desired time, the reaction mixture was cooled, and a small part of the solution was then poured into excess methanol to precipitate DhPVC. It was filtered and purified by reprecipitation, then dried under vacuum for 24 h. Excess piperidine in the main part of the dehydrochlorination solution of PVC was neutralized by acetic acid, and then Cu(I)Br/bpy (1/3 by mol) was added to the solution by stirring. After *t*BMA in a 50 times amount (by mole) of Cu(I)Br was also added to the solution, the mixture was refluxed under argon atmosphere for the desired time. At the end of the reaction time, the reaction mixture was filtered to remove undissolved particles, and the graft copolymer was precipitated from excess methanol, and dried under vacuum at 50°C for 24 h.

The dehydrochlorination of PVC was also carried out in the presence of sodium n-butoxide in THF at 25°C for 5 min. The excess base in the mixture was neutralized by acetic acid. DhPVC was grafted by ATRP with *t*BMA, and the grafted polymer was isolated as mentioned above.

In addition, dehydrochlorination of PVC was carried out in 1,3-dichlorobenzene at 95°C in the presence of piperidine as a base under an Ar atmosphere for 120 min. After DhPVC was isolated by precipitating in methanol, the graft copolymer was dissolved again in 1,3-dichlorobenzene, and was grafted by ATRP with *t*BMA at 95°C using Cu(I)Br/bpy as a catalyst.

As a comparison, the original PVC was also grafted with *t*BMA by ATRP refluxing in THF in the presence of CuBr/bpy as a catalyst.

2.3 Characterization

Gel permeation chromatography (GPC) was performed using an Agilant 1100 series instrument, which consisted of a pump, a refractive index detector and Waters Styragel columns, in THF. Polystyrene standards were used for calibration. NMR spectra were recorded using a Jeol FX 90Q spectrometer. FT-IR was measured using a Mattson 1000 spectrometer. Elemental analyses were carried out in the usual manner using a Leco 935 CHNS analyzer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data were obtained from a Shimadzu TGA-50 thermobalance and DSC-50, respectively.

3 Results and Discussion

3.1 Dehydrochlorination and Grafting

Partial dehydrochlorination of PVC generates new double bonds, and these may increase the amount of allylic chlorine atoms in the polymer backbone. Organic compounds containing allylic chlorine are used as an initiator in atom transfer radical polymerization (28).

HCl elimination was carried out from PVC in low ratio to perform grafting over allylic chlorine in partially dehydrochlorinated PVC (DhPVC). In the presence of the bases, dehydrochlorination of PVC in solution is expected to produce conjugated carbon-carbon double bonds along the polymer chain due to elimination of HCl (19). During dehydrochlorination of PVC, the color of the solution changed from colorless to yellow and dark brown. The results obtained from dehydrochlorination of PVC in the presence of piperidine in THF at 64°C and in 1,3-dichlorobenzen at 95°C, and in the presence of sodium n-butoxide in THF at 25°C, are shown in Table 1. HCl elimination in low ratio was preferred to avoid gelation during both grafting and elimination.

Grafting via ATRP on original PVC was first carried out to see the effect of partial dehydrochlorination on the grafting of PVC. During the conventional radical polymerization of vinyl chloride, structural defects such as allylic and tertiary chloride

Table 1. Dehydrochlorination of PVC

Polymer	Solvent/base	Temp. (°C)	Time (min)	Chlorine[a] (% wt)	Dehydrochl. (% by mol)
Original PVC	—	—	0	56.76	0
DhPVC	THF/piperidine	64	180	53.61	5.5
DhPVC(p)	1,3-Dichloro-benzen/piperidine	95	120	54.85	3.4
DhPVC(s)	THF/sodium-n-butoxide	25	5	55.10	2.9

[a] From the difference of carbon and hydrogen results in elemental analysis.

are introduced into the polymer, and their bond dissociation energies are relatively low, 58 and 67 kcal/mol, respectively (23). Under various conditions, grafting via ATRP over the labile chlorines on commercial PVC of many conventional vinyl monomers was reported (25, 26). In this study, the graft copolymerization on original PVC was carried out in THF as a solvent at reflux temperature (64°C in laboratory conditions) under argon atmosphere. A CuBr/bpy complex was used as catalyst. Assuming the presence of around 1% (by mol) labile chlorine in commercial PVC, the ratio of the macroinitiator (PVC)/CuBr/bpy/*t*BMA is used as 1/1/3/50 in the grafting, and the grafting was performed at three different times (17, 30 and 72 h).

Assuming forming of one allylic chlorine per eliminated HCl, the macroinitiator (DhPVC)/CuBr/bpy/*t*BMA ratio is used as 1/1/3/50. Atom transfer radical graft copolymerization (Scheme 1) is carried out at 64°C for 17, 30, 72 and 96 h. Grafting studies on DhPVC(p) and DhPVC(s) (they are described in Table 1) were performed similarly.

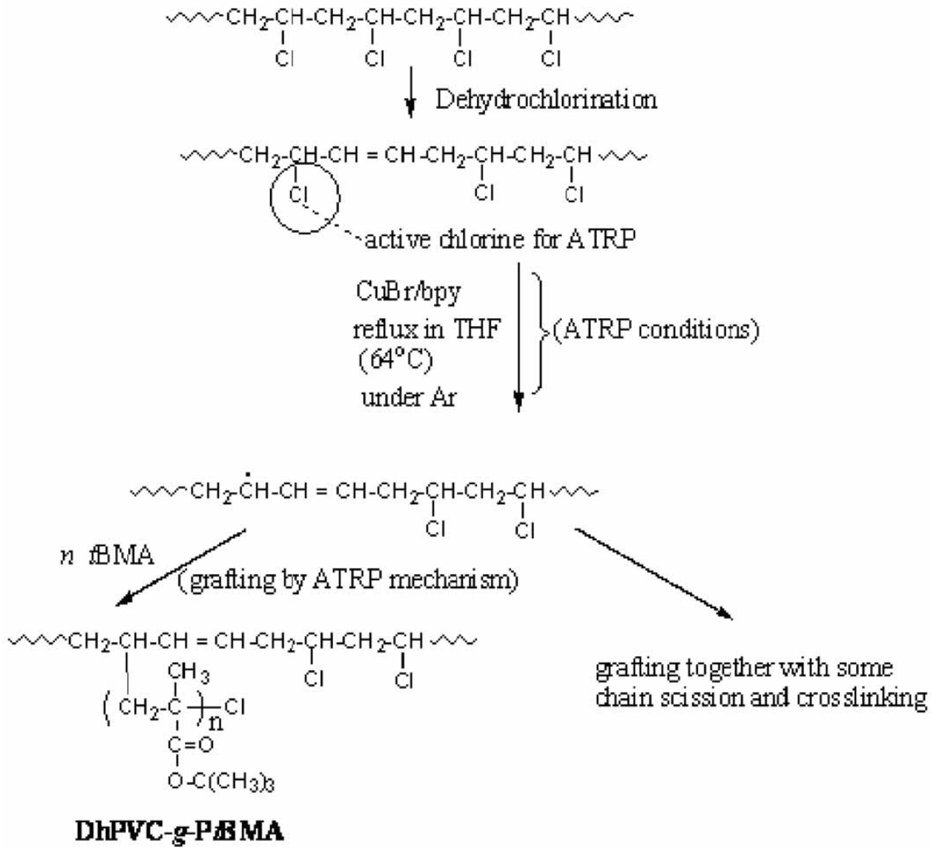
3.2 Structural and Molecular Weight Characterization

FTIR spectrum (Figure 1) of 5.5% dehydrochlorinated sample (DhPVC) shows a new broad band at 1634 cm^{-1} (C=C stretching vibration), a decrease in intensity of band at 763 cm^{-1} (C-Cl) in comparison with that of original PVC.

Average molecular weights and polydispersities of the graft copolymers are shown in Table 2. FTIR spectra of original PVC, dehydrochlorinated PVC, and some graft copolymers are shown in Figure 1. During the grafting, number average molecular weight increased from 75,500, which is that of the original PVC, to 82,000 up to 30 h, but it decreased to 57,900 in grafting for 72 h. The latter showed a small shoulder in the high molecular weight side of GPC trace, and this may result in growing chain ends during the grafting captured PVC chains.

During grafting, studies on DhPVC, number average molecular weight decreased from 69,500 to 26,400 depending on increasing grafting time and polydispersity increased around 2. A decrease in molecular weight during the grafting may be obvious evidence of main chain scission. The chain scission also increases the radical concentration in the grafting medium, and this event increases the polydispersity. These results indicated that atom transfer radical graft copolymerization on DhPVC is not well controlled due to radical production from another source. It is thought the double bonds in DhPVC have a role in the chain scission. GPC traces of all graft copolymers are unimodel except small shoulders in the high molecular weight side. These shoulders indicate that the grafting accompanied a small amount of crosslinking.

FTIR spectrum (Figure 1) of DhPVC-*g*-P*t*BMA (17 h) produced from the grafting of DhPVC with *t*BMA for 17 h



Sch. 1. Graft copolymerization of partially dehydrochlorinated PVC with *t*BMA.

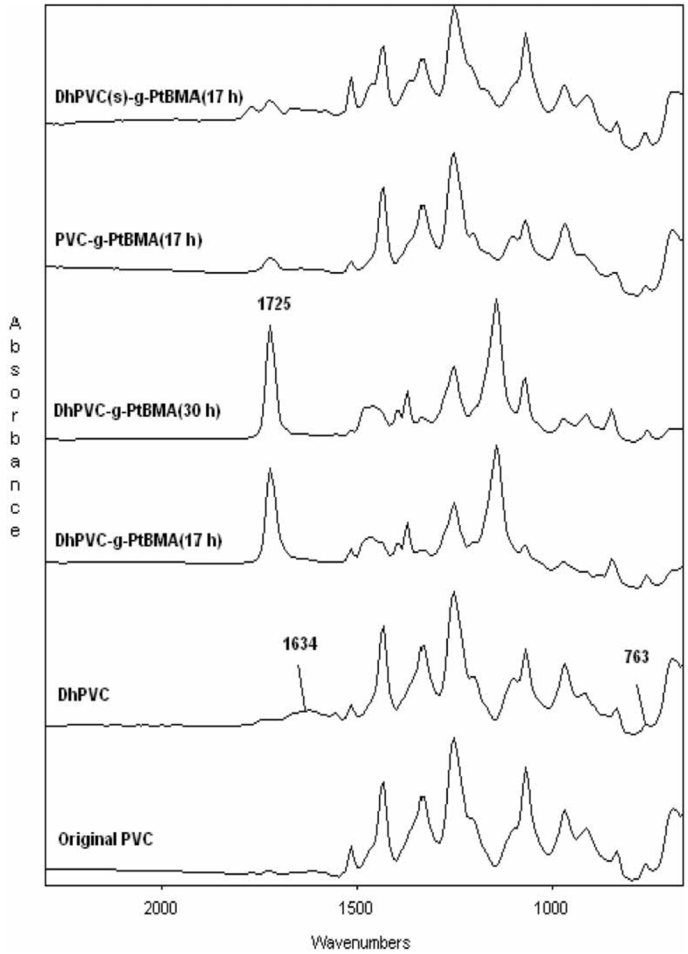


Fig. 1. FTIR spectra of some graft copolymers, DhPVC and original PVC.

evidently showed an ester carbonyl band at 1725 cm^{-1} and -(C═O)-O-C- symmetric stretching vibration at 1146 cm^{-1}, and these bands are relatively more intense in that product obtained in grafting for 30 h. These bands which are spectroscopic evidence of the grafting are very small in FTIR spectrum of PVC-*g*-P*t*BMA (17 h) produced from grafting original PVC with *t*BMA for 17 h. FTIR spectrum of the product obtained from the grafting of DhPVC(s) with *t*BMA for 17 h at 64°C also showed very small ester bands, and a very small band at 1775 cm^{-1} apart from ester bands. These results indicated that PVC, dehydrochlorinated in low ratio in THF at 64°C in the presence of piperidine, is a suitable material for grafting with *t*BMA via ATRP. The increasing of allylic structures by dehydrochlorination raised active centers as ATRP initiator, but these also caused chain scission during the grating.

Table 2. M_n and M_w/M_n values of the graft copolymers

Polymer	M_n	M_w/M_n	Grafting time (h)
Original PVC	75500	1.76	—
DhPVC	69500	1.98	—
PVC-*g*-P*t*BMA (17 h)	80500	1.60	17
PVC-*g*-P*t*BMA (30 h)	82000	1.66	30
PVC-*g*-P*t*BMA (72 h)	57900	1.82	72
DhPVC-*g*-P*t*BMA (17 h)	41000	1.88	17
DhPVC-*g*-P*t*BMA (30 h)	35000	2.03	30
DhPVC-*g*-P*t*BMA (72 h)	32300	2.14	72
DhPVC-*g*-P*t*BMA (96 h)	26400	1.99	96
DhPVC(p)-*g*-P*t*BMA (24 h)	59800	1.69	24

^{1}H-NMR and ^{13}C-NMR spectra of DhPVC-*g*-P*t*BMA (72 h) are shown in Figure 2. Signals at 1.43 ppm and 4.60 ppm in the ^{1}H-NMR spectrum describes methyl groups in *t*BMA of the graft copolymer and -CH(Cl)- groups in the PVC main chain, partially dehydrochlorinated, respectively. ^{13}C-NMR spectrum of the graft copolymer shows characteristic signals at 177.2 (C═O), 80.0 (-O-C), 56.0–58.0 (-CH(Cl)-), 45.8–47.4 (-CH_2- in the backbone), 27.7 [methyl carbon in -$C(CH_3)_3$] and 17.7 ppm (methyl carbon on *t*BMA chain).

A quantitative estimation on DhPVC-*g*-P*t*BMA (72 h) was done using the elemental analysis results (5.5%,

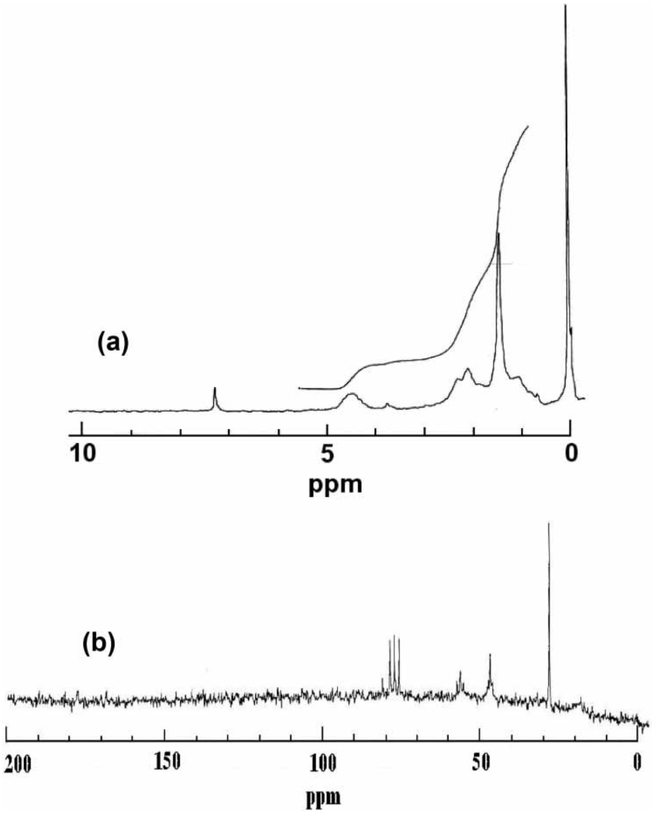


Fig. 2. ^{1}H-NMR (a) and ^{13}C-NMR, (b) spectra of DhPVC-*g*-P*t*BMA (72 h).

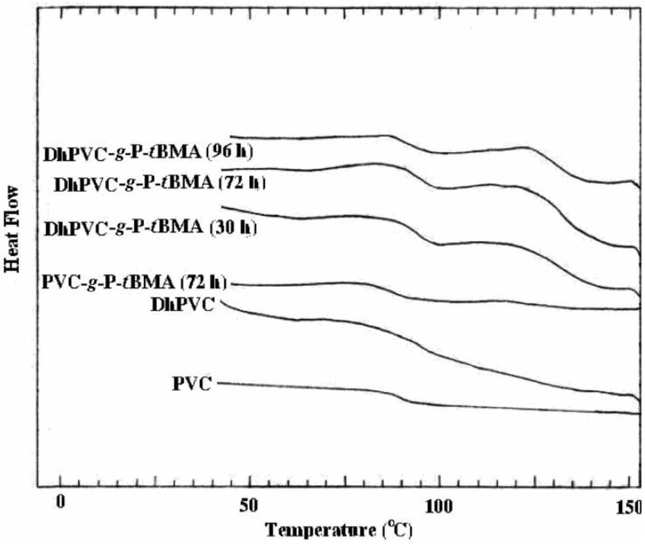


Fig. 3. DSC traces of some graft copolymers, DhPVC and original PVC.

by mol, dehydrochlorination), GPC data (M_n:32300) and integral heights of the signals at 1.43 ppm and 4.60 ppm. For this purpose, the following equations were used:

$$32300 = nx142 + 0.945x62.5 + mx26x0.055$$

$$\frac{mx0.945x1}{nx9} = \frac{9}{46}$$

Where n is the number of repeating units in the *t*BMA chain of the graft copolymer, m is number of repeating units in the PVC main chain of the graft copolymer, 142 and 62.5 are the molecular weighs of *t*BMA and vinyl chloride, respectively, and 9/46 is ratio of integral height of signal at 4.60 ppm to integral height of that at 1.43 ppm. The calculations show that m and n values are 239 and 127, respectively. In other words, there are 53 repeating units of P*t*BMA per 100 repeating units of PVC.

3.3 Thermal Characterization

DSC and TGA techniques were used to evaluate the thermal properties of the graft copolymers and starting polymers. While a T_g at 88°C was observed in the DSC scan (Figure 3) of the original PVC, a T_g at 114°C was observed in that of poly(*tert*-Butyl methacrylate), P*t*BMA, obtained by ATRP. DSC thermogram of 5.5% DhPVC showed a wide glass transition region with an inflexion point of 90°C. Thermal characteristics of all the polymers are summarized in Table 3. All the graft copolymers showed two glass transition temperatures that indicates phase separation. PVC-*g*-P*t*BMA (72 h) showed two glass transition points at 85 and 124°C, but the latter is less clear. The graft copolymers in rich *t*BMA units (DhPVC-*g*-P*t*BMAs) clearly showed two T_g at 92 and 128°C. This demonstrates the presence of phase separation in this graft copolymer. T_gs at 92°C and 128°C characterize DhPVC chains and P*t*BMA chains in the graft copolymer, respectively. Phase separation has also been reported in some graft copolymers obtained from the grafting of chloromethylated aromatic polyethersulfone with butyl acrylate and methyl acrylate (29), of modified polyethylene with styrene and methyl methacrylate (30), of poly(styrene-*co*-p-chloromethyl styrene) with ethyl methacrylate (31), and of PVC with 4-chlorostyrene (24). Although P*t*BMA homopolymer obtained by ATRP has a T_g at 114°C, P*t*BMA chains formed by the same method in the graft copolymer showed a higher T_g temperature (128°C). Because one end of P*t*BMA chains in the graft copolymer joined the DhPVC chain, these ends have a decreasing effect on the free volume and an increasing effect on the glass transition temperature. It has been reported that the main chain and side chain show a higher glass transition temperature than those of corresponding homopolymers in the graft copolymers occurring from phase separation. Poly(styrene)-*graft*-poly(ethyl methacrylate) showed two T_gs at 79–85°C and 103–105°C depending on grafting degree (31). The first value belongs to poly(ethyl methacrylate) and the second to poly(styrene), although poly(ethyl methacrylate) and poly(styrene) homopolymers show a glass transition at 65–70°C and about 100°C, respectively. In another study,

Table 3. Thermal properties of the polymers

Polymer	T_g (°C)	T_i^a (°C)	$T_{20\%}$ (°C)	$T_{50\%}$ (°C)	Residue at 400°C (%)
Original PVC	88	235^b	290	309	37
DhPVC	90	200	258	294	40
PVC-*g*-P*t*BMA (72 h)	85; 124	200	298	319	40
DhPVC-*g*-P*t*BMA (30 h)	92; 128	184	238	298	41
DhPVC-*g*-P*t*BMA (72 h)	92; 128	184	238	298	40
DhPVC-*g*-P*t*BMA (96 h)	92; 128	—	—	—	—
P*t*BMA	114	—	—	—	—

[a] Initial decomposition temperature.
[b] Temperature occurring rapidly of weight loss.

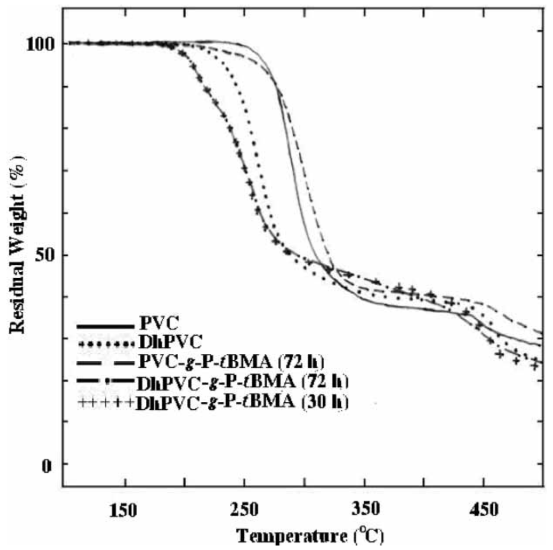


Fig. 4. TGA curves of three graft copolymers, DhPVC and original PVC.

original PVC and poly(4-chlorostyrene) homopolymers have a glass transition at 81°C and 119°C, respectively. The graft copolymer of these two polymers showed two T_gs at 83°C and 122°C (21).

The TGA results of three graft copolymers, DhPVC and the original PVC are summarized in Table 3, and traces of them are shown in Figure 4. If the initial decomposition temperature, T_i, has been assumed simply as a measurement of thermal stability, these temperatures are 235 and 200°C for the original PVC and DhPVC, respectively. Partially dehydrochlorination (5.5% by mol) of PVC generates new double bonds, and these increase the availability of allylic chlorine atoms in the polymer backbone. An increase of this kind of chlorine atoms decreases thermal stability of PVC. The grafting of PVC with *t*BMA also decreases thermal stability of PVC. The grafting on DhPVC also decreases thermal stability of DhPVC. It is well known (32, 33) that thermal degradation of radically prepared P*t*BMA started by formation of methacrylic acid units and by evolution of isobutylene from the side chain at around 190°C, and the degradation proceeded by formation of cyclic anhydride between nearby methacrylic acid units. In thermal degradation of DhPVC-*g*-P*t*BMA (30 and 72 h), proceeding of the decomposition above 300°C very slowly may be due to thermal stability of cyclic anhydride structures which occurred up to this temperature. Residue at 400°C of all the polymers investigated TGA data is in similar ratio (about 40%), although that of PVC is slightly lower (37%).

4 Conclusions

Partial dehydrochlorination (5.5% by mol) of PVC generates new double bonds, and these increase the availability of allylic chlorine atoms in the polymer backbone. This polymer, DhPVC, was used as a macroinitiator in ATRP, and its graft copolymerization with *t*BMA was carried out in THF at 64°C in the presence of CuBr/bpy as a catalyst. To compare grafting of original PVC was also studied under the same conditions. FTIR, NMR, DSC, TGA and elemental analyses results showed that *t*BMA units were bound to DhPVC in more ratio than that of the original PVC. Grafting was carried out probably together with some chain scission and a small amount of crosslinking.

5 References

1. Ravve, A. and Khamis, J.T. (1962) *J. Polym. Sci.*, **61**, 185.
2. Rao, S.P. and Santappa, M. (1968) *J. Polym. Sci. A.*, **16**, 95.
3. Walsh, D.J. and Sham, C.K. (1984) *Polymer*, **25**, 1023.
4. Kennedy, J.P. and Davidson, D.L. (1977) *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **30**, 13.
5. Toman, L., Spevacek, J., Holler, P. and Lucas, R. (1996) *Polymer*, **36**, 557.
6. Landler, J. (1960) *J. Polym. Sci.*, **48**, 477.
7. Fujiwara, H., Ishida, T., Taniguchi, N. and Wada, S. (1999) *Polym. Bull.*, **42**(**2**), 197.
8. Chapiro, A. and Matsumoto, A. (1962) *J. Polym. Sci.*, **57**, 743.
9. Chapiro, A. and Palma, G. (1967) *Eur. Polym. J.*, **3**, 151.
10. Gasparrini, G., Carenza, M. and Palma, G. (1980) *J. Polym. Sci., Polym. Lett. Ed.*, **18**, 29.
11. ElNasr, E.M., Dessouki, A.M. and AbdelBary, E.M. (1998) *Polym. Int.*, **46**, 150.
12. Feng, Y., Zhao, J.R., Wang, Q., Li, M. and Chen, X.F. (2000) *J. Appl. Polym. Sci.*, **75**, 475.
13. Marian, S. and Levin, G. (1981) *J. Appl. Polym. Sci.*, **26**, 329.
14. Huskic, M. and Sebenic, A. (1997) *J. Macmol. Sci., Pure Appl. Chem.*, **A34**, 1143.
15. Nakagawa, T., Hopfenberg, H.B. and Stannet, V. (1971) *J. Appl. Polym. Sci.*, **15**, 231.
16. Huskic, M., Roha, M., Harwood, H.J. and Sebenic, A. (1996) *Polym. Int.*, **40**, 227.
17. Guan, J.J. and Yang, W.J. (2000) *J. Appl. Polym. Sci.*, **77**, 2569.
18. Martinez, G., Santos, E. and Millan, J.L. (2001) *Macromol. Chem. Phys.*, **202**(**11**), 2377.
19. Ghaemy, M. and Gharaebi, I. (2000) *Eur. Polym. J.*, **36**, 1967.
20. Paik, H.J., Gaynor, S.G. and Matyjaszewski, K. (1998) *Macromol. Rapid. Commun.*, **19**, 47.
21. Percec, V., Popov, A.V., Castillo, E.R., Monterio, M., Barboiu, B., Weichold, O., Asendei, A.D. and Mitchell, C.M. (2002) *J. Am. Chem. Soc.*, **124**, 4940.
22. Asendei, A.D. and Percec, V. (2001) *J. Polym. Sci. Part A: Polym. Chem.*, **39**, 3392.
23. Endo, K. (2002) *Prog. Polym. Sci.*, **27**, 2021.
24. Percec, V. and Asgarzadeh, F. (2001) *J. Polym. Sci. Part A: Polym. Chem.*, **39**, 1120.
25. Percec, V., Cappotto, A. and Barboiu, B. (2002) *Macromol. Chem. Phys.*, **203**, 1674.
26. Bıcak, N. and Özlem, M. (2003) *J. Polym. Sci. Part A: Polym. Chem.*, **41**, 3457.
27. Chen, G., Zhu, X., Cheng, Z. and Lu, J. (2005) *J. Appl. Polym. Sci.*, **96**, 183.

28. Matyjaszewski, K. and Xia, J. (2001) *Chem. Rev.*, **101**, 2921.
29. Zhu, S., Xiao, G. and Yan, D. (2001) *J. Polym. Sci. Part A: Polym. Chem.*, **39**, 2943.
30. Matyjaszewski, K., Teodorescu, M., Miller, P.J. and Peterson, M.L. (2000) *J. Polym. Sci. Part A: Polym. Chem.*, **38**, 2440.
31. Coşkun, M. and Temüz, M.M. (2003) *J. Polym. Sci. Part A: Polym. Chem.*, **41**, 668.
32. Grassie, N., Johnson, A. and Scotney, A. (1981) *Eur. Polym. J.*, **17**, 589.
33. Hatada, K., Kıtayama, T., Fujimoto, N. and Nishiura, T. (1993) *J. Macromol. Sci., Pure and Appl. Chem.*, **A30**, 645.