Atom Transfer Graft Copolymerization of 2-Ethyl Hexylacrylate from Labile Chlorines of Poly(vinyl chloride) in an Aqueous Suspension

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ABSTRACT: Copper-mediated atom transfer radical polymerization (ATRP) is presented as a versatile tool for the graft copolymerization of 2-ethyl hexylacrylate with poly(vinyl chloride) (PVC) in an aqueous suspension. The appreciable solubility of PVC in 2-ethyl hexylacrylate (30%) at temperatures around 130 °C makes grafting of the monomer possible from labile chlorines of PVC in aqueous suspensions without the use of additional solvent. The first-order kinetics (rate constant \( k = 4.2 \times 10^{-6} \text{ s}^{-1} \)) of the mass percentage increase reveals a typical ATRP fashion of the graft copolymerization at low conversions. The use of a completely organosoluble copper(I) complex of hexylated triethylene tetramine, in combination with \( \alpha \)-methylcellulose as a stabilizer, makes the graft copolymerization possible in a dispersed organic phase. Nearly spherical, green particles can be obtained with moderate stirring rates (1000 rpm) in high graft yields. Although the kinetics of the reaction deviates from the first order at high conversions, reasonable graft yields (146%) can be attained within a reaction period of 24 h. In this study, the reaction conditions of the grafting have been studied, and graft products have been confirmed by common techniques such as \(^1\text{H} \) NMR, gel permeation chromatography, and differential scanning calorimetry. © 2006 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 44: 1900–1907, 2006

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INTRODUCTION

Copper-mediated atom transfer radical polymerization (ATRP) is one of the most important techniques for controlled living polymerizations.\(^1,2\) Controlled chain growth, a narrow molecular weight distribution, and the living nature of the polymerization are apparent peculiarities of the method. The living behavior of the polymerization allows many block\(^3,4\) and graft copolymers\(^5\) to be prepared with well-defined structures.

Copper-mediated ATRP, on the other hand, is unique, especially in graft copolymerization, because only trace quantities of free homopolymer formations are observed during grafting.\(^6\) In other words, chain-transfer reactions are greatly suppressed in the process. As a result, ATRP, when used in a grafting-from process, does not yield free homopolymer as undesired byproducts.

The advantage of the method in practice is avoiding the loss of a waste amount of the monomer in grafting. Because of this advantage, the method is also applicable even in grafting from solid surfaces.\(^7–9\)

This work deals with the graft copolymerization of poly(vinyl chloride) (PVC) in aqueous sus-
pensions by ATRP. The graft copolymerization of PVC prepolymer has been found to be attractive for imparting a plasticizing effect. Although the vinyl chloride/vinyl acetate copolymer is a commercial product that is being sold under the name of self-plasticized PVC, grafting from pre-existing PVC is of importance to attain materials with different mechanical and chemical properties. Because chlorines of PVC are chemically inert, these cannot be considered initiation sites for grafting from PVC by the ATRP method.

The first report on the use of the ATRP technique for the grafting of PVC is associated with starting from a PVC copolymer containing minute amounts of vinyl chloroacetate as a comonomer. Replaceable chlorines of the comonomer have been used as initiation sites for grafting by ATRP.

Most chlorine atoms of PVC itself are too inert to initiate ATRP for grafting from the polymer backbone. However, commercial PVC has been demonstrated to have a few percent of labile chlorines, which arise from structural defects forming during the radical polymerization of vinyl chloride.

Detailed investigations of Percec’s group confirmed the presence and formation mechanism of the labile chlorines of PVC.

Although the reliability of the analytical method given by Caraculacu et al. for the determination of the labile chlorines is doubtful, we believe that those might be as high as 4%.

The labile chlorines can be considered reactive enough to initiate ATRP for grafting from nonmodified PVC. Recently, Percec and coworkers showed that naked PVC can be grafted by copolymerization with various vinyl monomers from the labile chlorines. Soon afterwards, we demonstrated that highly plasticizing monomers butyl acrylate and 2-ethyl hexyl acrylate (EHA) can also be grafted efficiently from PVC in 1,2-dichlorobenzene as a solvent at 90 °C.

The labile chlorines of PVC prepared by ATRP may also cause complications in making its block copolymers. Percec’s group described a versatile method for preparing ABA-type triblock copolymers containing PVC as the B block. In this method, PVC having iodo groups in both ends is used as the initiating site for block copolymerization with various vinyl monomers, by ATRP, under relatively mild conditions.

Suspension polymerization of water-immiscible monomers is mostly attractive industrially because water is used as the reaction medium. The use of ATRP in aqueous suspensions makes it a viable method for large-scale controlled polymerizations. However, the extension of ATRP to the suspension process is a difficult task because of its limitations, such as the water solubility of the copper complexes and the ligands involved. The emulsion polymerization mechanism becomes favored for water-soluble copper complexes, and smaller particles, instead of suspension particles, form, being a few hundred micrometers in diameter.

There appear to be few reports dealing with ATRP in aqueous suspensions. Matyjaszewski’s group reported that ATRP in the presence of an oil-soluble ligand, 4,4′-di(5-nonyl)-2,2′-bipyridine, proceeded with first-order kinetics, and this was ascribed to a suspension mechanism. Additionally, the ATRP of a methyl methacrylate/dimethylacrylate mixture in an aqueous suspension of diphenyl ether has been reported to give cross-linked, spherical bead particles about 50–100 μm in diameter. The solubility of the copper complex catalyst in the organic phase is crucial to performing ATRP in aqueous suspensions. In our previous work, we demonstrated that hexylated triethylene tetramine (H-TETA) forms oil-soluble copper complexes and provides true suspension conditions in the ATRP of methyl methacrylate.

To the best of our knowledge, no reports have been published on the application of ATRP in graft copolymerization in aqueous suspensions so far. In fact, grafting in a suspension by ordinary initiation methods is not a successful approach because of large quantities of free homopolymer formed as a byproduct. In one of the successful reports, styrene was graft-copolymerized in a suspension from thiol containing chitin in high yields. In another publication, the graft copolymerization of vinyl chloride monomer from poly (butyl acrylate) in suspension has been demonstrated to give soft polymers.

Here we report for the first time the use of ATRP for the grafting of EHA from PVC in an aqueous suspension. In this work, H-TETA has been chosen as a proper ligand because it is hydrophobic enough to extend ATRP for grafting in aqueous suspensions. Another requirement is an additional solvent to dissolve the prepolymer to be grafted. Fortunately, PVC is highly soluble in this monomer around 130 °C, and this makes grafting possible without the use of additional solvent. Because all the prerequisites for a successful grafting in a suspension were being fulfilled, we thought that ATRP could work in the graft copolymerization of EHA from labile chlorines of PVC in an aqueous suspension.
In this study, the characteristics and kinetics of the graft copolymerization have been studied, and the structures of the graft products have been investigated by conventional techniques such as NMR, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC).

**EXPERIMENTAL**

**Materials**
Commercial EHA (Fluka) was rendered inhibitor-free via shaking with a 0.1 M NaOH solution before the graft copolymerization. All the other chemicals—the suspension stabilizer, z-methylcellulose (Aldrich), PVC (number-average molecular weight \( M_n = 22,000 \), polydispersity index (PDI) = 1.95; Aldrich), and solvents—were analytical-grade commercial products. They were used without any further purification.

**Cuprous Bromide**
This was freshly prepared by a method described in the literature.

**Preparation of H-TETA**
The ligand H-TETA (hexacis-1,1,4,7,10,10-hexyl-1,4,7,10-tetraazadecane according to the International Union of Pure and Applied Chemistry) was prepared by the reaction of 1-bromohexane with triethylene tetramine as reported elsewhere.

**Graft Copolymerization of EHA in an Aqueous Suspension**
To a 250-mL, three-necked flask equipped with a reflux condenser and a nitrogen inlet, 20.8 mL (0.1 mol) of EHA (inhibitor-free) and 3.125 g of PVC (0.05 mol of repeat units) were added under a nitrogen atmosphere. The flask was placed in a thermostated oil bath at 130 °C. The mixture was stirred with a magnetic bar until a clear solution was obtained (ca. 40 min). The temperature of the oil bath was adjusted to 90 °C. Meanwhile, a stock solution of z-methylcellulose was prepared by the dissolution of 0.5 g of z-methylcellulose in 200 mL of distilled water. This solution (100 mL) was heated to boiling and added to the flask with vigorous stirring under a nitrogen flow. The stirring rate was adjusted to 1000 rpm.

The ligand H-TETA (0.325 g, \( 5 \times 10^{-4} \) mol) and CuBr (0.071 g, \( 5 \times 10^{-4} \) mol) were added, and the nitrogen inlet was closed. The mixture was stirred for a predetermined time interval. Droplets of the polymer solution became green in about 5 min and turned brown. The kinetics of the grafting was followed by the repetition of this procedure for various time intervals. The reaction content was poured into 500 mL of cold water and filtered. The gel-like flakes were filtered, dispersed in 30 mL of acetic acid, and filtered. The crude products were washed with 30 mL of ethanol. The products were finally dried at 40 °C in vacuo for 48 h and weighed.

Those graft products were light green because of the copper salts remaining. For the viscosity, NMR, and GPC analyses, colorless samples were obtained separately by the procedure described next.

**Techniques**
The molecular weights of the graft samples were monitored by GPC. Before the manipulations, the copper residues in the samples were removed by reprecipitation twice in acetic acid/water mixtures (1/1). Thus, approximately 0.2-g light blue samples were dissolved in 10 mL of tetrahydrofuran (THF) and precipitated in 40 mL of acetic acid/water mixtures. The samples, dried in vacuo at 40 °C for 24 h, were white and pure enough to use in NMR and GPC measurements.

\(^1\)H NMR spectra were recorded with a Bruker 250-MHz spectrometer (250 MHz for \(^1\)H) in dimethyl sulfoxide-\(d_6\).

Gel permeation chromatograms were recorded with an Agilent 1100 series instrument consisting of a pump, a refractive-index detector, and Waters Styragel (HR4, HR3, and HR2) columns. THF was used as an eluent at a flow rate of 0.3 mL/min.

With DSC, the glass-transition temperatures (\( T_g \)’s) of the polymers were measured with a TA DSC Q10 model instrument in a flowing nitrogen atmosphere at a heating rate of 10 °C/min.

Infrared spectra were taken with a Perkin-Elmer Spectrum One Fourier transform infrared (FTIR) spectrometer.

The viscosities were determined by a capillary viscometer technique with an Ubbelohde viscometer.

**RESULTS AND DISCUSSION**
A few percent of labile chlorines existing in commercial PVC serve as initiation sites for atom
transfer graft copolymerization (Scheme 1), as reported previously.\textsuperscript{18}

Here we present the graft copolymerization of EHA with PVC in an aqueous suspension by ATRP. Interestingly, PVC ($M_n = 22,000$ Da) is soluble in EHA at temperatures around $130^\circ C$. Notably, upon cooling to room temperature, the solution becomes gelled again. When the gel is heated up to $100^\circ C$, a homogeneous solution is obtained, again implying physical gelation. The solubility of PVC in the monomer at elevated temperatures allows performing graft copolymerization in a suspension without the use of additional solvent. The monomer EHA was chosen to induce a plasticizing effect due to the low $T_g$ of the corresponding homopolymer ($-84^\circ C$) and its compatibility with PVC.

**Grafting**

A viscous solution of PVC in EHA is quite dispersible in hot water containing 0.25% $\alpha$-methylcellulose as a suspension stabilizer. The grafting is effected by the addition of CuBr and the ligand (in 1/1/50 [CuBr]/[H-TETA]/[EHA] molar ratios) to the suspension stirred at 90 °C.

An immediate coloration of the organic phase takes place in 5 min. Only slightly white turbidity is observed in the aqueous phase throughout the polymerization. This behavior indicates that CuBr is being extracted to the organic phase by H-TETA, almost quantitatively, at this temperature, in accordance with our previous report.\textsuperscript{24}

This may be considered a visual confirmation of true suspension conditions provided by H-TETA.

At the end of predetermined reaction times, the graft product in the organic phase was precipitated in acetic acid, which is a nonsolvent for PVC and EHA homopolymer. Acetic acid was chosen to remove the unreacted monomer as well as copper residues without changing the particle shapes of the graft products.

However, the products isolated in this way were still greenish.

**Kinetics**

The graft yields (Fig. 1) based on the total monomer consumption indicate nearly first-order kinetics with a rate constant of $k = 4.2 \pm 0.24 \times 10^{-6}$ s\(^{-1}\) for yields below 126%. This can be ascribed to controlled chain growth for low graft.

![Figure 1. First-order kinetic plot for the graft copolymerization of EHA in an aqueous suspension (at 90 °C for a 1/1/50/100 [H-TETA]/[CuBr]/[PVC]/[EHA] molar ratio).](image)
yields. However, at high conversions, the semilogarithmic plot greatly deviates from linearity. Such a deviation from the first order is common for ATRP at high conversions. A molecular weight/conversion plot of the grafting (Fig. 2) also gives a nearly linear relationship at low conversions but deviates above 20% monomer consumption. The obtained PDIs are rather high (Table 1) in comparison with those for the homopolymerizations in ATRP. This might be largely due to the high PDI (1.95) of the starting PVC. Nearly spherical particles were obtained for reaction times longer than 6 h, whereas shorter times resulted in sticky and shapeless particles because of the presence of a large amount of unreacted monomer.

Structure

Copper-free test samples for GPC analyses and spectral measurements were prepared separately by reprecipitation of the THF solutions in acetic acid twice. Simple evidence for the incorporation of graft chains into the PVC structure is the characteristic stretching vibration bands of the carbonyl group of the EHA component appearing at 1723 cm\(^{-1}\) in their FTIR spectra (Fig. 3). In the spectra, other typical peaks of each component can also be observed.

The \(^1\)H NMR spectrum (Fig. 4) of the graft copolymer sample (from a 5-h reaction with a 2/1 monomer ratio) shows proton signals for both PVC and EHA polymer.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction Time (h)</th>
<th>Graft Yield (% w/w)</th>
<th>(M_n^a)</th>
<th>(M_w)</th>
<th>PDI</th>
<th>Inherent Viscosity (dL/g)(^b)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.0</td>
<td>22.000</td>
<td>43.000</td>
<td>1.95</td>
<td>0.278</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>14.0</td>
<td>36.900</td>
<td>69.700</td>
<td>1.88</td>
<td>0.285</td>
</tr>
<tr>
<td>3</td>
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<td>16.1</td>
<td>38.100</td>
<td>71.600</td>
<td>1.87</td>
<td>0.287</td>
</tr>
<tr>
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<td>3</td>
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<td>40.000</td>
<td>72.200</td>
<td>1.80</td>
<td>0.310</td>
</tr>
<tr>
<td>5</td>
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<td>33.5</td>
<td>40.700</td>
<td>71.900</td>
<td>1.77</td>
<td>0.318</td>
</tr>
<tr>
<td>6</td>
<td>8</td>
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<td>1.99</td>
<td>0.362</td>
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<td>16</td>
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<td>2.29</td>
<td>0.470</td>
</tr>
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<td>24</td>
<td>146.0</td>
<td>76.300</td>
<td>171.000</td>
<td>2.24</td>
<td>0.477</td>
</tr>
</tbody>
</table>

\(^a\) From GPC.
\(^b\) In a dimethylformamide solution (1 g/dL) at 25 ± 1 °C.
Thus, the broad multiplet located in the 3.7–4.7 ppm range represents methine (–CH–Cl) protons of PVC and –OCH₂—protons of the EHA grafts. Two methyl protons of 2-ethyl hexyl units give a triplet around 1 ppm. The multiplet in 1.8–2.6 ppm is due to methylene protons of

Figure 3. FTIR spectrum of a graft copolymer sample (entry 3). % T = transmittance.

Figure 4. ¹H NMR spectrum of a PVC-g-EHA sample (entry 5).
PVC and \(-\text{CH}—\text{COO}—\) protons of the polymerized EHA component. The multiplets at 1.2–1.7 ppm arise from all the other CH\(_2\) protons of the 2-ethyl hexyl group.

The integral ratio of the multiplets at 3.7–4.7 ppm to those of the other proton signals is 0.31. By neglecting end-group effects and effects of chemical shifts at the graft points, we find that this corresponds to 31.2% (w/w) grafting. This value fairly agrees with that obtained by a mass increase (33.5%).

The copper-free samples give no soluble fraction in ethyl acetate, and this indicates the absence of the free homopolymer of EHA; this is similar to the case for the grafting in the solvent 1,2-dichlorobenzene as described before.\(^{15}\) This is an important aspect of ATRP graft methodology in comparison with the other techniques yielding free homopolymers as byproducts. Indeed, GPC traces (Fig. 5) present unimodal peaks for each sample, and this is direct evidence for the presence of only grafted species in the samples.

We have also studied the effects of different monomer ratios (i.e., \([\text{EHA}]/[\text{PVC}] = 1/1, 1.5/1, 2/1, 2.5/1,\) or \(3/1\)). The graft yields were almost the same for the reaction times shorter than 5 h. However, the kinetic plots showed great deviations from first-order kinetics for the monomer ratios lower than 2/1. For instance, for the 1/1 ratio, the graft yield was 52% after 6 h. However, the yield did not change practically for prolonged reaction times. This must have been due to rapidly increasing viscosities inside the droplets. For the higher monomer ratios, the droplets were still soft and sticky because of unreacted monomer absorption. However, the presence of unreacted monomer is not desirable in suspension polymerization processes. For this reason, the monomer ratio of 2/1 was chosen as the optimum ratio.

**DSC**

What we expected by grafting with EHA was to bring a plasticizing effect to PVC. To inspect such an effect, we compared DSC traces of PVC and one of the graft samples (the product of 3 h of reaction; Fig. 6). \(T_g\) of PVC at 85 °C shifts to 58 °C after grafting (upper curve). Although further detailed studies are needed for clarifying such effects, this result shows that the graft segments are reasonably compatible with PVC and that the plasticization is being well established.

**CONCLUSIONS**

The solubility of PVC in EHA at elevated temperatures makes the graft copolymerization of this
monomer possible from the labile chlorines of commercial PVC in an aqueous suspension without the use of an organic solvent.

Beaded products can be obtained in high graft yields by the proper adjustment of the stirring rates and the stabilizer concentrations. This work reveals that the presented method seems to be applicable to the large-scale grafting of PVC in aqueous suspensions.

From an industrial viewpoint, the preference is the highest graft yields to minimize unreacted monomer to be recovered. However, the loss of chain-growth control at high graft yields can be considered a disadvantage of this procedure. Nevertheless, this procedure might still be useful, even in this case, because the grafting is achieved without the formation of free homopolymers, which cannot be attained by other methods.

The only drawback of this procedure is greenish graft products, a common problem in copper-mediated ATRP.

REFERENCES AND NOTES