Hydrogen-transfer polymerization of vinyl monomers derived from \(p\)-tolyl isocyanate and acrylamide derivatives

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Received 11 December 1997; received in revised form 22 January 1998; accepted 6 February 1998

Abstract

The anionic polymerization of \(N\)-acryloyl-\(N\)\(^9\)-\(p\)-tolylurea (1) was carried out at 80\(^\circ\)C in \(N,N\)-dimethylformamide (DMF), dimethylsulfoxide (DMSO), acetonitrile or toluene containing \(N\)-phenyl-\(\beta\)-naphthylamine (1 mol.\%) as a radical inhibitor for 24 h using \(t\)-BuOK or 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) (3 mol.\%) as an initiator. It was found that 1 undertook selectively the hydrogen-transfer polymerization in the case of \(t\)-BuOK as an initiator but both hydrogen-transfer and vinyl polymerization proceeded in the case of DBU. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Tolyl isocyanate; Acrylamide; Hydrogen-transfer polymerization

1. Introduction

Since Matlack et al. first reported the hydrogen-transfer polymerization of acrylamide using anionic initiators, various unsaturated amides have been evaluated for their effectiveness on the hydrogen-transfer process in the polymerization [1–6]. Unlike simple vinyl polymerization systems, the hydrogen transfer polymerization is most useful in production of functionalized main chains. We have recently reported the hydrogen-transfer polymerization of \(N\)-acryloyl-\(N\)-\(p\)-toluenesulfonfonylurea and \(N\)-acryloyl-\(N\)'-(4-methylbenzoyl)urea prepared from acrylamide and activated isocyanates (i.e. \(p\)-toluenesulfonyl isocyanate and 4-methylbenzoyl isocyanate, respectively) [7–10]. As they have two acidic protons on the nitrogen atoms, their anionic polymerizations involved the hydrogen-transfer process and functional groups such as \(-CO–N(CONHX)–\) and \(-CO–NH–CO–N(X)–\) (\(X: SO_R^2\) and \(-COR\) for \(N\)-acryloyl-\(N\)\(^{-}\)-\(p\)-toluenesulfonfonylurea and \(N\)-acryloyl-\(N\)'-(4-methylbenzoyl)urea, respectively) can be incorporated into the main chains of the polymers.

\(N\)-Acryloyl-\(N\)'-tolylurea (1) has a urea moiety with two amide protons on the nitrogen atoms. The different acidity of the NH groups in 1 may have an interesting influence on the
hydrogen-transfer polymerization behavior. The polymerization of monomer 1 will offer polymers with unique functional groups (i.e. –CO–N(CONHR)– and/or –CO–NH–CO–N(R)–) in the main chain which may be of importance for new functional polymers. Accordingly, we wish to describe detailed results on the hydrogen-transfer polymerization of 1 and 2 (an N-methylated form of 1) (Scheme 1).

2. Experimental

2.1. Materials and instruments

1,8-Diazabicyclo[5,4,0]undec-7-ene (DBU), dimethylformamide (DMF), dimethylsulfoxide (DMSO), and acetonitrile (MeCN) were dried over CaH₂, distilled, and stored under nitrogen. Toluene (PhMe) was dried over sodium metal and distilled under nitrogen atmosphere. Potassium tert-butoxide (t-BuOK) was prepared from t-butanol and potassium. Other commercially available reagents were used without further purification.

IR spectra were measured on a JASCO FT/IR-5300 spectrometer. ¹H-NMR and ¹³C-NMR spectra were recorded on a JEOL JNM-EX90 (¹H-NMR: 90 MHz, ¹³C-NMR: 22 MHz) or JEOL JNM-EX400 (¹H-NMR: 400 MHz, ¹³C-NMR: 100 MHz) spectrometer. Number- (Mₙ) and weight-average (Mₜ) molecular weights and molecular weight distributions (Mₙ/Mₜ) were estimated by gel permeation chromatography (GPC) on a Tosoh Co. HLC-8020 system equipped with polystyrene gel columns (TSK® gel G6000HXL, TSK® gel G5000HXL, TSK® gel G4000HXL and TSK® gel G2500HXL)
Table 1
Hydrogen-transfer polymerization of N-acryloyl-N'-p-tolylurea 1

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Initiator</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Conv. (%)</th>
<th>Yield (%)</th>
<th>M (M/M/M)</th>
<th>x/y/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>t-BuOK</td>
<td>DMF</td>
<td>80</td>
<td>24</td>
<td>60</td>
<td>16</td>
<td>3100 (1.19)</td>
<td>37/63/0</td>
</tr>
<tr>
<td>2</td>
<td>t-BuOK</td>
<td>DMF</td>
<td>80</td>
<td>72</td>
<td>72</td>
<td>27</td>
<td>3200 (1.07)</td>
<td>36/64/0</td>
</tr>
<tr>
<td>3</td>
<td>t-BuOK</td>
<td>DMF</td>
<td>120</td>
<td>24</td>
<td>66</td>
<td>20</td>
<td>3400 (1.08)</td>
<td>28/72/0</td>
</tr>
<tr>
<td>4</td>
<td>t-BuOK</td>
<td>DMSO</td>
<td>80</td>
<td>24</td>
<td>58</td>
<td>14</td>
<td>2800 (1.23)</td>
<td>35/65/0</td>
</tr>
<tr>
<td>5</td>
<td>t-BuOK</td>
<td>MeCN</td>
<td>80</td>
<td>24</td>
<td>62</td>
<td>16</td>
<td>2800 (1.21)</td>
<td>33/67/0</td>
</tr>
<tr>
<td>6</td>
<td>t-BuOK</td>
<td>PhMe</td>
<td>80</td>
<td>24</td>
<td>28</td>
<td>2</td>
<td>3500 (1.24)</td>
<td>47/53/0</td>
</tr>
<tr>
<td>7</td>
<td>DBU</td>
<td>DMF</td>
<td>80</td>
<td>24</td>
<td>63</td>
<td>20</td>
<td>2900 (1.27)</td>
<td>30/43/27</td>
</tr>
<tr>
<td>8</td>
<td>DBU</td>
<td>DMSO</td>
<td>80</td>
<td>24</td>
<td>59</td>
<td>11</td>
<td>3000 (1.25)</td>
<td>23/44/33</td>
</tr>
<tr>
<td>9</td>
<td>DBU</td>
<td>MeCN</td>
<td>80</td>
<td>24</td>
<td>68</td>
<td>17</td>
<td>1900 (1.32)</td>
<td>37/42/21</td>
</tr>
<tr>
<td>10</td>
<td>DBU</td>
<td>PhMe</td>
<td>80</td>
<td>24</td>
<td>72</td>
<td>14</td>
<td>2200 (1.46)</td>
<td>39/39/22</td>
</tr>
</tbody>
</table>

\(^{\text{a}}\)Conditions: [1] = 1 M, initiator (3 mol.%), inhibitor: N-phenyl-β-naphthylamine (1 mol.%).

\(^{\text{b}}\)The ratio of \(x, y\) to \(z\) in Scheme 2, determined by \(^{1}\)H-NMR spectra.

\(^{\text{c}}\)EtO-insoluble part.

\(^{\text{d}}\)Estimated by GPC based on polystyrene standards, eluent: DMF containing LiBr (5.8 mM).

using DMF containing LiBr (5.8 mM) as eluent, a flow rate of 1.0 ml/min, polystyrene calibration, and an ultraviolet (UV) detector. Fast atom bombardment mass spectra (FAB/MS) were recorded by using a JEOL JMS-700 spectrometer, whereby a mixture of a sample and \(m\)-nitrobenzyl alcohol on a standard FAB target was subjected to a beam of xenon atoms produced at 6 keV, 2 mA.

2.2. Synthesis of N-acryloyl-N'-p-tolylurea (1)

The method described for N-acryloyl-N'-phenylurea was used with slight modifications [11]. To a 500-ml round-bottomed flask containing a 250-ml benzene solution of acrylamide (13.3 g, 0.190 mol) was added \(p\)-tolyl isocyanate (25.0 g, 0.190 mol) under nitrogen. After refluxing for 44 h under nitrogen atmosphere, the mixture was cooled to room temperature to precipitate a white solid, which was recrystallized from benzene. Yield 73% (26.1 g, 0.140 mol), m.p. 169–170°C.

IR (KBr): 3399 (NH), 1705 (C=O), 1690 (C=O) cm\(^{-1}\); \(^{1}\)H-NMR (CDCl\(_3\), 90 MHz) \(\delta\): 2.32 (s, 3H, \(\text{CH}_3\)–C\(_6\)H\(_5\)–), 5.88 (dd, \(J = 9.23\) and 2.60 Hz, 1H, \(\text{CH}_2\)=CH– cis), 6.33 (dd, \(J = 16.79\) and 9.23 Hz, 1H, \(\text{CH}_2\)=CH–), 6.60 (dd, \(J = 16.79\) and 2.60 Hz, 1H, \(\text{CH}_2\)=CH– trans), 7.13 (d, \(J = 8.51\) Hz, 2H, –C\(_6\)H\(_5\)=–), 7.42 (d, \(J = 8.51\) Hz, 2H, –C\(_6\)H\(_5\)=–), 10.59 (bs, 1H, –CONHPh–), 10.77 (bs, 1H, –CONHCO–) ppm. \(^{13}\)C-NMR (CDCl\(_3\), 22.4 MHz), \(\delta\): 20.8, 120.4, 129.5, 129.7, 130.8, 134.0, 134.4, 152.8, 166.7 ppm. Anal. calc'd for C\(_{13}\)H\(_{16}\)N\(_2\)O: C, 64.69%; H, 5.92%; N, 13.72%. Found: C, 64.38%; H, 5.67%; N, 13.66%.

2.3. Synthesis of N-acryloyl-N-methyl-N'-p-tolylurea (2)

To a 200-ml round bottomed flask containing a 100-ml DMF suspension of Na\(_2\)S\(_2\)O\(_3\) (55 wt.% in oil) (2.14 g, 49.0 mmol) was added N-acryloyl-N'-p-tolylurea (1, 10.0 g, 49.0 mmol) under nitrogen. After stirring at room temperature for 24 h, methyl iodide (34.8 g, 245 mmol) was added and the mixture was stirred at ambient temperature for 7 days. The resulting mixture was extracted with diethyl ether following the addition of water. The organic phase was washed three times with an Na\(_2\)S\(_2\)O\(_3\) aqueous solution, dried over MgSO\(_4\), and evaporated to dryness. The residue was purified by chromatography on silica gel with hexane–chloroform (v/v 1/3) as eluent to isolate the N'-methylated...
monomer (2). Yield 41% (4.39 g, 20.11 mmol), m.p. 78–79°C.

IR (KBr): 3436 (NH), 1705 (C=O), 1655 (C=O) cm\(^{-1}\); \(^1\)H-NMR (CDCl\(_3\), 90 MHz) \(\delta\): 2.29 (s, 3H, CH\(_3\)-C\(_6\)H\(_4\)-), 3.36 (s, 3H, CH\(_3\)-N-), 5.86 (dd, \(J = 9.45\) and 2.79 Hz, 1H, CH\(_2\)=CH- cis), 6.43 (dd, \(J = 16.83\) and 2.79 Hz, 1H, CH\(_2\)=CH- trans), 6.72 (dd, \(J = 16.83\) and 9.45 Hz, 1H, CH\(_2\)=CH-), 7.10 (d, \(J = 8.51\) Hz, 2H, -C\(_6\)H\(_4\)-), 7.41 (d, \(J = 8.51\) Hz, 2H, -C\(_6\)H\(_4\)-), 11.44 (s, 1H, -CONHPh-) ppm; \(^1^3\)C-NMR (CDCl\(_3\), 22.4 MHz), \(\delta\): 20.7, 31.7, 120.3, 128.9, 129.3, 131.1, 133.5, 135.1, 152.2, 169.6 ppm. Anal. calcd for C\(_{12}\)H\(_{14}\)N\(_2\)O: C, 66.04%; H, 6.47%; N, 12.84%. Found: C, 66.02%; H, 6.32%; N, 12.78%.

2.4. Hydrogen-transfer polymerization (typical procedure)

The monomer (1 or 2) (1.0 M), an initiator (t-BuOK or DBU, 3 mol.%), and N-phenyl-β-
naphthylamine (1 mol.%, an inhibitor for radical polymerization) were dissolved in DMF, DMSO, MeCN or PhMe in a test tube under nitrogen atmosphere. After the reaction at 80 °C for 24 h, the mixture was poured into diethyl ether and the precipitated polymer was dried in vacuo.

2.5. Polymer obtained from 1 (in Table 1, run 1)

IR (KBr): 3426 (NH), 2975 (–CH2–), 1696 (C=O), 1466 (–CH3–), 1385 (C–N), 763 (–CH2–) cm⁻¹; 1H-NMR (CDCl3, 400 MHz) δ 2.25–2.45 (s, 3H × 0.73, CH3–C6H4–), 2.60–
3.55 (m, 2H, –CH₂–CH₃–CO–), 3.55–4.50 (m, 2H, –N–CH₂–CH₂–), 6.95–7.45 (m, 4H, 2H, –C₆H₄–), 7.08 (d, J = 5.80 Hz, 2H, –C₆H₄–), 7.11 (d, J = 8.00 Hz, 2H, –C₆H₄–), 7.31 (d, J = 8.00 Hz, 2H, –C₆H₄–), 3.50–4.50 (m, 2H, –N–CH₂–CH₂–), 2.25–2.78 (m, 1H, –CH₂–CH₂–), 2.78–3.50 (m, 2H, –CH₂–CH₂–), 2.62–2.78 (m, 1H, –CH₂–CH₂–), 10.01 (bs, 1H, –CONHPh–), 10.33 (bs, 1H, –CONHCO–) ppm; ¹³C-NMR (DMSO-d₆, 100 MHz) δ 20.35, 20.41, 20.66, 30.74, 31.16, 32.35, 33.0, 34.20, 34.65, 35.13, 35.75, 36.41, 36.92, 37.67, 38.07, 119.11, 119.31, 119.57, 128.44, 128.97, 129.29, 129.70, 131.96, 132.11, 132.53, 135.07, 136.45, 136.55, 136.92, 128.21, 128.54, 129.93, 130.18, 131.94, 134.66, 134.77, 135.07, 136.45, 136.55, 148.62, 148.65, 169.19 ppm; FAB/MS m/z 338 [M + H]⁺.

3. Results

3.1. Hydrogen-transfer polymerizations of 1 and 2

The polymerization of 1 was carried out at 80°C for 24 h using t-BuOK (3 mol.%) as an initiator in DMF containing N-phenyl-β-naphthylamine (1 mol.%) as a radical polymerization inhibitor (Scheme 2). As a result, conversion of 1 reached to 60% and a polymer 3 (Mₙ = 3100) was obtained as a diethyl ether-insoluble part in 16% yield (Table 1, run 1).

From the ¹H-NMR spectrum of the obtained polymer, the hydrogen-transfer polymerization was found to proceed exclusively (Fig. 1a). That is, peaks attributable to the methylenes adjacent to the nitrogen atom and those adjacent to the carbonyl group were observed at δ 3.55–4.50 ppm (d, f) and 2.60–3.55 ppm (e, g) respectively. The ratio of the two hydrogen-transfer units (x:y in Scheme 2) was determined by the integral ratio of the residual amide protons observed at 10.34 and 10.01 ppm. The peak area of the aromatic protons was smaller than that of the expected structure by 27%. It may be assumed that aromatic parts are eliminated from the monomer and/or the polymer. Actually, TLC analysis of the diethyl ether-soluble part showed several UV active spots and, 1,3-di(4-methylphenyl)-1,3,5-triaza-2,4,6-trioxocyclooctane (4) was isolated in 6% (Table 1, run 5).

One possible explanation of the path generating 4 is shown in Scheme 3. That is, the propagating N-anion attacks the carbonyl group in y unit...
or the monomer, and the N-anion (a) generated by the deprotonation of the monomer attacks the imide carbonyl group in y unit or another monomer to give b. Then, the NH proton adjacent to the tolyl group of b is deprotonated again to generate the N-anion (c). The intramolecular cyclization of c leads to the production of d which converts to 4 by the protonation.

To increase the polymer yield, the polymerization was carried out for a longer period (i.e. 72 h) (run 2). As a result, the conversion of 1 increased to 72%, and polymer 3 was obtained in 27% yield ($M_n = 3100$). When the polymerization of 1 was carried out at higher temperature (i.e. 120°C), the conversion increased slightly to give 3 in a little better yield (run 3). However, the elimination of the tolyl group was more obvious than the polymer obtained in run 1 (the deficit of tolyl group: run 1, by 27%; run 3, by 40%). These results indicated that side reactions eliminating low-molecular-weight compounds from the monomer and/or the polymer may be accelerated at higher reaction temperature. Although the difference of the polymer structure depended slightly on the solvents, the hydrogen-transfer polymerization of 1 was selectively carried on with t-BuOK regardless of the solvents (runs 1, and 4–6).

Scheme 4 shows the plausible process of the polymerization, in which an N-anion (ia and/or ib), initially generated from monomer 1 by t-BuOK, attacks another monomer to afford an anion (ii) [12]. The anion (ii) may be subsequently transformed to two kinds of N-anions (iii and iv) through the hydrogen-transfer process and the polymer chain may grow in this way.

In contrast to the case of t-BuOK, polymers containing both the hydrogen-transfer and the vinyl polymerization units were obtained when DBU was used as an initiator. For instance, in the $^1$H-NMR spectrum of the polymer obtained in run 7 (Fig. 1b), the peaks attributable to methyne and methylene protons of the vinyl polymerization unit at $\delta$ 1.65–2.25 ppm together with those due to the hydrogen-transfer polymerization unit ($\delta$ 2.60–4.50 ppm) were observed. The proportion of the vinyl polymerization was evaluated from the relative peak area ($z = 21–33\%$) (runs 7–10 in Table 1), which seems to be also independent of the solvents. The counter cation (the protonated form of DBU) may be less interactive to the propagating end than the case of t-BuOK. Consequently, the nucleophilicity of the propagating end might become strong enough to induce the vinyl polymerization.

In order to exclude one of the two active hydrogens in the hydrogen-transfer polymerization, monomer 2 was prepared from 1 with methyl iodide and was subjected to the polymerization under the same conditions. However, no polymer was produced using both t-BuOK and DBU. The TLC analysis of the reaction mixture revealed a lot of spots, but none of these compounds could be isolated by column chromatography or HPLC. In our previous work, N-acryloyl-N-methyl-N'-p-toluenesulfonylurea and N-acryloyl-N-methyl-N'-(4-methylbenzoyl)urea were subjected to the anionic polymerization, which did not provide polymers but low molecular-weight compounds. In these cases, reverse reactions to the monomer synthetic paths took place and the resulting isocyanates gave some adducts [7–10]. Although we could not detect any products supporting the similar side reactions, the poor polymerizability of 2 might be due to its instability.

4. Conclusions

Under the anionic polymerization conditions, monomer 1 prepared from tolyl isocyanate with acrylamide was found to undergo hydrogen-transfer polymerization. The selectivity of the hydrogen-transfer to the vinyl polymerization was found to be effected not significantly by the solvents but by the initiators. Monomer 1 polymerized selectively via the hydrogen-trans-
fer process using t-BuOK as the initiator, while that of DBU conducted both the hydrogen-transfer and the vinyl polymerization.

References

[12] As the initiation step, two possibilities might be taken into consideration. Those are the nucleophilic addition of t-BuO toward the unsaturated bonds of 1 and the deprotonation of the amide proton by t-BuO-. In our previous reports (ref. 7 and 8), we could support that the hydrogen-transfer polymerization of N-acryloyl-N'-p-toluenesulfonylurea (CH=CHCONHTs) proceeds via the latter path (i.e. the deprotonation from N±H), by isolating an initiating salt (i.e. CH=CHCON TsK). In the ²H-NMR spectrum of polymer 3, no peak attributable to t-butoxy end was observed, while peaks of terminal double bonds could be detected. Thus, the latter path might be also plausible as the initiation step in the polymerization of 1, as shown in Scheme 3.