Acylation of Polybutadiene Containing 4-Phenyl Urazole

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ABSTRACT

Polybutadiene with a narrow molecular weight is synthesized by anionic polymerization of butadiene monomer in cyclohexane at 20 °C using n-butyl-lithium as initiator. This polymer is statistically functionalized with 4-phenyl-1,2,4-triazoline-3,5-dione by hydrogen abstraction addition reaction (ene reaction) in an extent of 5, 10, and 15%. These functionalized polymers are reacted with acetyl chloride as well as benzoyl chloride in presence of pyridine at room temperature. These reactions lead to the replacement of N—N with acetyl and benzoyl groups. The amount of urazole and acyl incorporation are determined by 1H NMR technique. Some physical properties of these modified polybutadienes are reported.

Key Words: polybutadiene, ene reaction, 4-phenyl-1,2,4-triazoline-3,5-diones, inherent viscosity, acylation

INTRODUCTION

Homopolymers and copolymers of a large number of polydienes such as random cis-trans-polybutadiene, cis-polybutadiene, 1:1 alternating copolymer of furan and maleic anhydride, random styrene (45%)-butadiene, SBR containing of 25% styrene and styrene-butadiene random copolymer, styrene-butadiene ABA block copolymer, styrene-isoprene block copolymer, 15% styrene-poly-cis-isoprene, polycrilonitrile-co-butadiene, and poly-1,2-butadiene have been reacted with 4-phenyl and 4-methyl-1,2,4-triazoline-3,5-diones [1—3]. The reactions occur at ambient temperature, and an extent of chemical conversion ce up to 93% is obtained.

The modification of polydienes with other triazolinediones has been studied by Stadler and co-workers [4—9] in details.

The urazole derived from the ene reaction of triazolinediones with alkenes and polydienes has one N—H proton, which seems to be very acidic. The acidity of this proton has been measured and is quite acidic with pKₐ of 4.71 which is almost the same as that of acetic acid [10].

4-Substituted-urazoles are converted to 1-acyl derivatives by acylation reaction with a series of carboxylic anhydrides [11]. A simplified procedure for the N-acylation of oxazoline-2-one chiral auxiliaries is also reported [12].

Recently we have been able to take advantage of these acidic N—H in a compound, 1-methyl-2,5-bis-(4-phenylurazoyl)pyrrole and synthesize
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novel polymers via N-alkylation and N-acylation reactions [13 and 14].

The aim of this investigation has been to synthesize polybutadiene containing 4-phenyl urazole and to examine its reaction with acid chlorides, for the preparation of new functionalized polybutadiene.

EXPERIMENTAL

Materials and Equipments
Reagents are purchased from Fluka, Aldrich, and Riedel-deHaen AG Chemical Companies.

4-Phenyl-1,2,4-triazoline-3,5-dione, Ph.TAD, was prepared by a reported procedure [15]. The proton nuclear magnetic resonance (1H NMR, 90 MHz) spectra are recorded on a Varian EM-390 instrument. Multiplicities of proton resonances are designated as singlet (s), doublet (d), multiplet (m) and broad (br), and tetramethysilane (TMS) is used as an internal reference.

IR spectra are recorded on Shimadzu 435 IR spectrophotometer. The spectra of the oil and liquids have been obtained neat by a smear on sodium chloride pellets. Vibrational transition frequencies are reported in wavenumber (cm⁻¹), and band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br).

Inherent viscosities have been measured by a standard procedure using a Cannon Fensk Routine Viscometer.

Synthesis of Polybutadiene
Polybutadiene with a molecular weight of 50,000 (PB-50) and polydispersity of 1.040 (by GPC analysis) was prepared by anionic polymerization in cyclohexane at room temperature using n-butyl-lithium as initiator. The polymer contains 90% 1,4-polybutadiene (mixture of cis and trans isomers) and 10% 1,2-polybutadiene which were determined by 1H NMR technique by the ratio of peaks area of 2 and 3 (Figure 1).

Reaction of PB-50 with 4-Phenyl-1,2,4-triazoline-3,5-dione at 5% Conversion
Into a 250 mL round-bottomed flask 0.90 g (1.81×10⁻⁵ mol) of PB-50, compound (1), and 100 mL of methylene chloride were added. The reaction mixture was covered with a black plastic bag and then stirred at room temperature for 2 h. To this clear solution was added dropwise a deep-red colour of 0.15 g (8.35×10⁻⁴ mol) of compound (2) Ph.TAD in 10 mL of methylene chloride. The clear solution was stirred overnight. The solvent was removed under reduced pressure up to about 5 mL. Then it was added to 100 mL isopropanol containing a few crystals of hydroquinone as antioxidant. The polymer was precipitated immediately. At the end, the solution was decanted and the resulted modified polymer was dried under vacuum to give 0.99 (94.5%) pale yellow gummy
polymer (3). IR (neat) NaCl cell: 3150 (s,sh), 2900 (s), 2850 (s), 1764 (m), 1700 (s,br), 1640 (m), 1600 (w), 1500 (m), 1420 (s,br), 1345 (w), 1280 (w,br), 1238 (w), 1130 (w), 1070 (w), 960 (s), 910 (m), 760 (m), 720 (m,br), 690 (m) cm$^{-1}$; $^1$H NMR (CDCl$_3$, TMS): $\delta$ 1.68–2.43 (s, br, 6H), 4.89–6.06 (m, br, 5H), 7.28–7.76 (s, br, 5H) ppm (Figure 2).

This reaction was repeated to prepare modified polybutadienes with 10 and 15% by weight of (2).

**Preparation of Acetylated Polybutadiene at 5% Conversion**

Into a 100 mL round-bottomed flask were placed 0.11 g of polymer (3) and 30 mL of tetrahydrofuran (THF). The suspension mixture was stirred at room temperature for overnight, then 0.1 mL (1.41×10$^{-3}$ mol) of pyridine was added. Acetyl chloride (4) (0.1 mL, 1.41×10$^{-3}$ mol) in 5 mL of THF was added to the above solution and it was stirred for overnight. The solvent was removed under reduced pressure and low temperature (40–45 °C) up to about 3 mL. Then it was added to 30 mL of isopropanol containing a few crystals of 2,6-di-tert-butyl-4-methyl phenol as antioxidant. The polymer was precipitated immediately. At the end, the solution was decanted and the resulted modified polymer was dried under vacuum and it gave 0.11 g (96.9%) of yellow gummy polymer (6). IR (neat) NaCl cell: 2900 (s), 2850 (s), 1765 (s), 1730 (s,br), 1638 (m), 1600 (m), 1500 (s), 1410 (s,br), 1280 (w,br), 1130 (w), 1065 (w), 1020 (w), 960 (s), 910 (s), 760 (s), 730 (s), 690 (m), 630 (w,br) cm$^{-1}$; $^1$H NMR (CDCl$_3$, TMS): $\delta$ 1.720–2.319 (s,br, 9H), 4.78–5.91 (m,br, 5H), 7.27–7.74 (s,br, 5H) ppm (Figure 3).

This reaction was repeated to prepare polymers with 10 and 15% by weight of acetyl chloride.

**Preparation of Benzoylated Polybutadiene at 5% Conversion**

Into a 100 mL round-bottomed flask were placed 0.097 g of polymer (3) and 30 mL THF. The suspension mixture was stirred at room temperature for overnight, then 0.07 mL (8.62×10$^{-4}$ mol) of pyridine was added. Benzoyl chloride (5) (0.1 mL, 8.62×10$^{-4}$ mol) in 5 mL of THF was added to the above solution and it was stirred for overnight. The solvent was removed under reduced pressure and low temperature (40–45 °C) up to about 3 mL.
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Then it was added to 30 mL of isopropanol containing a few crystals of 2,6-di-tert-butyl-4-methyl phenol as antioxidant. The polymer was precipitated immediately. At the end, the solution was decanted and the resulted modified polymer was dried under vacuum and it gave 0.10g (97.8%) of yellow gummy polymer (7). IR (neat) NaCl cell: 2900 (s), 2850 (s), 1770 (m), 1710 (s), 1638 (m).

Figure 3. $^1$H NMR (90 MHz) spectrum of acylated PB-50 containing 4-phenyl-1,2,4-triazoline-3,5-dione (2) in CDCl$_3$ at room temp. (6a): 5% modification, (6b): 10% modification, and (6c): 15% modification. Peak at position 1 is related to the saturated CH$_2$, peaks at 2 and 3 are related to the vinylic protons and at 4 is related to the phenyl protons.

Figure 4. $^1$H NMR (90 MHz) spectrum of benzoylated PB-50 containing 4-phenyl-1,2,4-triazoline-3,5-dione (2) in CDCl$_3$ at room temp. (7a): 5% modification, (7b): 10% modification, and (7c): 15% modification. Peak at position 1 is related to the saturated CH$_2$, peaks at 2 and 3 are related to the vinylic protons and at 4 is related to the phenyl protons.
This reaction was repeated to prepare polymers with 10 and 15% by weight of benzoyl chloride.

RESULTS AND DISCUSSION

The reaction of PB-50 (1) with 5, 10 and 15% by weight of freshly sublimed PhTAD (2) was performed in methylene chloride at room temperature with high yield (>90%) as presented in Table 1.

Upon addition of PhTAD to a methylene chloride solution of PB-50, the red colour of PhTAD disappeared, and showed the reaction proceeds immediately via an ene reaction (Scheme I). The fading time increased by increasing the concentration of PhTAD toward PB-50 (Table 1).

The \(^1\)H NMR spectra of the modified polymers (3a), (3b) and (3c) showed peaks at the same position of PB-50 because the main fraction of polymer (3) is the PB skeleton but we have a new peak at 7.28–7.76 ppm which was assigned to the phenyl protons of urazole group. Peaks at 4.85–6.06 ppm and 7.28–7.76 ppm, both indicate five protons, but differences in peak area is related to the differences between modified and unmodified repeating unit, then from eqn (1) the percentage modification is calculated:

\[
\text{Modification\%} = \frac{\text{peak area at 7.36–7.83 ppm}}{\text{peak areas: 7.63–7.83 ppm + 4.83–6.07 ppm}} \times 100
\]

The inherent viscosity of unmodified polybutadiene (PB-50) in chloroform was 0.778 dL/g, whereas that of 5, 10, 15 w% modified polymers were found to be 0.3034, 0.2073 and 0.1448 dL/g, respectively (Table 1). In general, the inherent viscosity decreases as the percentage of the incorporation of the polar urazole pendant group increases. This is due to the intramolecular interaction between the urazole moiety. This interaction causes the modified polymers to contract and show a drastic change in their molecular sizes.

The reaction of acetyl and benzoyl chloride with modified polymers (3a), (3b) and (3c) lead to the formation of acylated polymers (6a)–(6c) and (7a)–(7c) at room temperature (Scheme II). Dissolution time increases by increasing the percentage of modification (Tables 2 and 3).

The data in Tables 2 and 3 indicate that by increasing the concentration of the bulky entering group (acid chloride), although N–H interaction was omitted but because of polar interactions, viscosity decreased.

Table 1. Modification of polybutadiene with PhTAD in methylene chloride solution.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Fading of PhTAD (min)</th>
<th>Yield (%)</th>
<th>Modification (%)</th>
<th>Inherent viscosity*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Calculated</td>
<td>Observed</td>
</tr>
<tr>
<td>(3a)</td>
<td>4</td>
<td>94.51</td>
<td>5</td>
<td>5.79</td>
</tr>
<tr>
<td>(3b)</td>
<td>5</td>
<td>96.30</td>
<td>10</td>
<td>10.55</td>
</tr>
<tr>
<td>(3c)</td>
<td>10</td>
<td>96.40</td>
<td>15</td>
<td>15.18</td>
</tr>
</tbody>
</table>

* Measured at a concentration of 0.5g/dL in CHCl₃ at 25°C.
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Polymer 3 + RCOCl

\[
\text{Pyridine} \quad \frac{\text{THF}}{} 
\]

\[
\text{Ph} \quad \text{(3a): } 5\% \quad \text{R: CH}_3 \quad \text{(6) or (7a) } 5\%
\]

\[(3b): 10\% \quad \text{R: Ph} \quad \text{(6) or (7b) } 10\%
\]

\[(3c): 15\% \quad \text{(6) or (7c) } 15\%
\]

Scheme II

The 'H NMR spectrum of the modified polymers (7a), (7b) and (7c) showed an enhancement at the aromatic protons regions, which were assigned to the phenyl group of benzoyl chloride and phenyl group protons of urazole. Peaks at 4.81–5.89 ppm and 7.29–7.72 ppm indicate 5 and 10 protons, respectively. So to calculate the percent modification, the peak area at 4.81–5.89 ppm must be divided by 5 and that of 7.29–7.72 ppm must be divided by 10, then by using eqn (1) the modification percentage are obtained.

When modification reactions were performed with acid chlorides (4) and (5), the inherent viscosity decreases as the percentage of the incorporation of the polar acyl pendant group increases (Figure 5). This is due to the interaction between the polar pendant groups.

CONCLUSION

Polybutadiene modified with PhTAD can be

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Dissolution time</th>
<th>Yield (%)</th>
<th>Modification (%) Calculated</th>
<th>Modification (%) Observed</th>
<th>Inherent viscosity'</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6a)</td>
<td>THF</td>
<td>overnight</td>
<td>96.89</td>
<td>5</td>
<td>5.13</td>
<td>0.3054</td>
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<tr>
<td>(6b)</td>
<td>THF</td>
<td>24 h</td>
<td>88.49</td>
<td>10</td>
<td>10.7</td>
<td>0.1362</td>
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<tr>
<td>(6c)</td>
<td>THF</td>
<td>36 h</td>
<td>97.24</td>
<td>15</td>
<td>15.9</td>
<td>0.1041</td>
</tr>
</tbody>
</table>

* Measured at a concentration of 0.5g/dL in CHC\textsubscript{3} at 25 °C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Dissolution time</th>
<th>Yield (%)</th>
<th>Modification (%) Calculated</th>
<th>Modification (%) Observed</th>
<th>Inherent viscosity'</th>
</tr>
</thead>
<tbody>
<tr>
<td>(7a)</td>
<td>THF</td>
<td>overnight</td>
<td>97.81</td>
<td>5</td>
<td>5.2</td>
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</tr>
<tr>
<td>(7b)</td>
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<td>24 h</td>
<td>78.79</td>
<td>10</td>
<td>9.6</td>
<td>0.2053</td>
</tr>
<tr>
<td>(7c)</td>
<td>THF</td>
<td>36 h</td>
<td>99.70</td>
<td>15</td>
<td>15.5</td>
<td>0.1670</td>
</tr>
</tbody>
</table>

* Measured at a concentration of 0.5g/dL in CHC\textsubscript{3} at 25 °C.
readily converted to acylated polymers by acylation reaction. The amount of conversion can be controlled both by the amount of PhTAD and acylating reagents. Furthermore, one can easily use a wide variety of the optically active acid chlorides and readily convert the polybutadiene containing urazole groups to the optically active polymers. This is also a new method for the preparation of functionalized polymers.

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**REFERENCES**