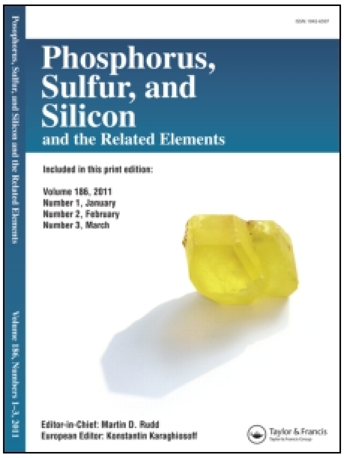

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Synthesis and Thermal Properties of Monodispersed Telechelic Diols Prepared from Radical Telomerization of Undecylenol with Novel Dithiols

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SYNTHESIS AND THERMAL PROPERTIES OF MONODISPERSED TELECHELIC DIOLS PREPARED FROM RADICAL TELOMERIZATION OF UNDECYLENOL WITH NOVEL DITHIOLS.

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Abstract The synthesis of novel monodispersed telechelic diols from the radical telomerization of undecylenol with new α,ω-dithiols was investigated. These diols are semi-crystalline and exhibit a thermal stability much higher than that of commercially available polydispersed diols.

INTRODUCTION

Monodispersed telechelic (or α, ω -difunctional) oligomers are very important intermediates for the preparation of well defined structure polymers[1-5], and especially the diols which are precursors of polyesters or polyurethanes leading to several applications : chain-extenders, paints and coatings, composites, liquid crystals, release paper, protection for metal etc.

RESULTS AND DISCUSSION

The synthesis of novel monodispersed sulfurated telechelic diols (B,x) is demonstrated. Firstly, novel long chain α, ω -dithiols (A, x) were prepared from the dropwise addition of commercially available nonconjugated dienes onto commercial dithiols[6] whereas a batch mixture of these reactants gave a polydispersed blend of dithiols separable with difficulties. On the other hand, a dropwise addition of dithiol onto a large excess of nonconjugated diene led to a new α,ω-diene[7]. Then the radical bistelomerization of undecylenol onto dithiols A produced the diol B selectively and quantitatively, according to the following scheme[8] :

$$HS(CH_2)_2O(CH_2)_2SH \ + \ H_2C{=}CH{-}(CH_2)_x{-}CH{=}CH_2 \longrightarrow \underline{A,x}$$

$HS(CH_2)_2O(CH_2)_2S(CH_2)_{x+4}S(CH_2)_2O(CH_2)_2SH$ A,x

$\downarrow$ $H_2C=CH-(CH_2)_9-OH$/peroxides

$HO(CH_2)_{11}-S(CH_2)_2O(CH_2)_2S(CH_2)_{x+4}S(CH_2)_2O(CH_2)_2S(CH_2)_{11}-OH$ B,x

Both these diols were characterized by ^1H and ^{13}C-NMR.

On the other hand, α,ω-mercapto alcohol $HSC_2H_4OC_2H_4S(CH_2)_{11}OH$ obtained by monoaddition of the bis(2-mercapto ethyl) ether onto the undecylenol[9], reacted onto commercially available dienes to produce the diol a selectively. However, in this latter case, the yields were 70-75%.

These diols show a semi-crystalline behaviour : T_m = 64°C (B,2) or 34°C (B,6) and T_g = 12°C (B,2) or 10°C (B,6). The thermogravimetric analyses (Figure 1) show these monodispersed diols exhibit a much better thermal stability (of about 60-80°C) than that of the commercially available non sulfurated polydispersed diols of about the same molecular weight, such as poly (THF) which is regarded as one of the most stable polyethers.

In addition, recent investigations have shown that the mechanical properties of a Polyurethane (PU) prepared from monodispersed α,ω-diol were much better than those of a PU obtained from a polydispersed commercially available diol[10].

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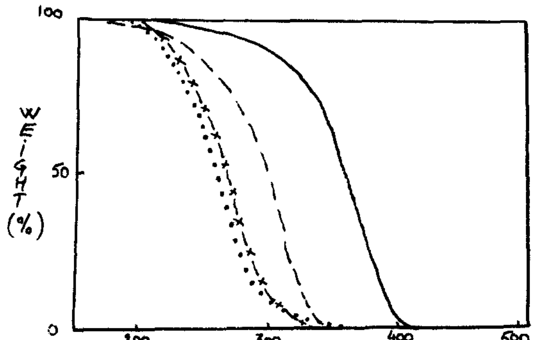

FIGURE 1 Thermogravimetric curves of PEG 10,000 (.....), PEG 1,000 (-x-x-x), Terathane 650 (dotted line) and diol B,6 (full line).