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Registry No. 1, 33827-81-5; aluminum oxide, 1344-28-1; oxygen, 7782-44-7; nitrogen, 7727-37-9.

Polymeric Blocked Isocyanates by Reductive Carbonylation of Nitropolystyrene

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Polymeric isocyanates and their precursors of controlled molecular weight and degree of functionality are important building blocks in powder coating formulations.[1-3] Metal carbonyl induced reductive carbonylation of nitroaromatics has been explored as a phosgene-free route for the preparation of isocyanates and blocked isocyanates.[4-6] Application of carbonylation methodology to nitro-substituted oligomers or polymers represents a novel route to polymeric cross-linkers with no intermediacy of phosgene or low-molecular-weight isocyanates. Besides, the information available on the chemical reactions of polymers suggests that polymeric substrates may be useful in distinguishing homogeneous and heterogeneous catalysts.[8,9] We report here the use of the $Ru_3(CO)_{12}/NEt_4^+Cl^-$ system for the reductive carbonylation of nitro-substituted polystyrene.

A typical experimental protocol for the reductive carbonylation of nitropolystyrene (**2**) is as follows.[5,6] Polystyrene (**1**) was nitrated with HNO_3/H_2SO_4 at 0 °C, and the degree of nitration was estimated by nitrogen analysis.[10] Nitropolystyrene (0.5 g) (elemental analysis: C, 56.24 (64.4) N, 9.03 (9.39); H, 4.69 (4.27) ($n = 1$)) in toluene/methanol (25 mL) was allowed to react with CO (450 psi) at 160-170 °C in a 200-mL autoclave in the presence of $Ru_3(CO)_{12}$ (0.156 mmol) and $NEt_4^+Cl^-$ (1.09 mmol) for 6 h. The proposed reaction pathway (I) is presented in Figure 1.

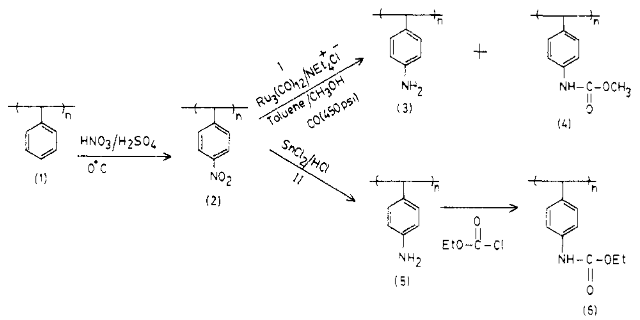

Figure 1. Synthesis of polymer-bound blocked isocyanates.

Table I
$Ru_3(CO)_{12}/NEt_4^+Cl^-$-Induced Carbonylation of Nitropolystyrene

substrate	catalyst	conv, %	selectivity,[a] % Ⓟ–NCO	 Ⓟ–NH_2	 Ⓟ–NHCOOR
Ⓟ–NO_2[b]	$Ru_3(CO)_{12}/NEt_4^+Cl^-$ toluene/methanol	100		60	40
Ⓟ–NO_2[b]	$Ru_3(CO)_{12}/NEt_4^+Cl^-$ acetonitrile/methanol	90		70	25
Ⓟ–NO_2[b]	$Ru_3(CO)_{12}$ toluene/methanol	80		80	
Ⓟ–NO_2[b]	$Ru_3(CO)_{12}$ acetonitrile	100	trace	80	
Ⓟ–NO_2[c]	$Ru_3(CO)_{12}/NEt_4^+Cl^-$ toluene/methanol	100		50	50
Ⓟ–NO_2[c]	$Ru_3(CO)_{12}/NEt_4^+Cl^-$ acetonitrile/methanol	95		60	40

[a] Experimental conditions: temperature, 170 °C; pressure, 450 psi of CO; time, 6 h. Percentages of products refer to weight fractions of the polymers. [b] Polystyrene M_w = 60 000 and degree of substitution $n = 1$. [c] Polystyrene M_w = 10 000 and degree of substitution $n = 0.5$.

$Ru_3(CO)_{12}$ has been found to be an effective catalyst in toluene/acetonitrile/methanol at 170 °C and 400-450 psi of CO for the reductive carbonylation of nitropolystyrene. Table I summarizes the results of carbonylation experiments under various conditions. In most cases, complete conversion was achieved with the disappearance of nitro groups (1535, 1350 cm^{-1}). Typically, the reaction yielded a mixture of **3** and **4**. The molecular weight and degree of nitration were found to be critical in achieving good solubility of the samples and influenced conversions and selectivities. In general, an increased level of nitration resulted in poor solubility of the polymer and lower selectivities. The conversions and selectivity were dependent on the solubility of the nitropolymers, presence of cocatalyst, and the nature of solvent mixture. Removal of $NEt_4^+Cl^-$ and ROH resulted in total conversion to **3**. Carbamate formation was detected by the presence of a carbonyl peak at 1720 cm^{-1}. It was

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further confirmed by subjecting **4** to thermal deblocking at 200 °C, which results in isocyanate (2260 cm^{-1}) formation. The identity of compounds **3** and **4** was established by a two-step parallel synthesis(II) of **5** and **6** and similarities of IR spectra. However, compound **3** also shows peaks at 1680 cm^{-1}, corresponding to urea linkages. Thus the product profile results are similar to that of nitrobenzene leading to carbamate, aniline, and diphenylurea.[5] Collman[11] proposed the method to differentiate homogeneous and heterogeneous hydrogenation catalysts based on their reactivity toward polymeric substrates. Only the soluble molecular catalysts have been found to interact with functional groups attached to insoluble polymer networks. The present work is an extension of carbonylation reaction to polymeric substrates and may be indicative of a truly homogeneous nature of the catalysts.

Our methodology offers a novel phosgene-free, isocyanate-free route to polyurethane coatings and provides a new formulation latitude. The reaction conditions have not been optimized. The key variables in the design of polymeric cross-linker are (1) backbone composition, (2) molecular weight, and (3) functionality. Clearly, the metal carbonyl/cocatalyst system has a very significant influence on the reaction pathway.[12]

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Registry No. $NEt_4^+Cl^-$, 56-34-8; methanol, 67-56-1; $Ru_3(CO)_{12}$, 15243-33-1.

Communications to the Editor

Chain-Transfer Agents for Living Ring-Opening Metathesis Polymerization Reactions of Norbornene

Catalysts of the type M(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (M = Mo[1] or W[2]) have now been used to polymerize norbornene,[3] 5,6-disubstituted norbornadienes (stereoselectively),[4] and 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene[5] by living ring-opening metathesis polymerization (ROMP).[6] Living ROMP requires that a propagating alkylidene complex react only with monomer, not with the substituted double bonds in the polymer chain. Up to now, the living polymer has been quenched with an aldehyde in order to remove the metal and cap the polymer in a Wittig-like reaction. A chain-transfer (CT) agent for these relatively unreactive complexes would be much more desirable. An initial search for a suitable CT agent focused on substituted cyclopentenes.[7] These chain-transfer agents were relatively unsuccessful because the cyclopentene bond was not reactive enough relative to a double bond in a side chain. We now find that 1,3-dienes and styrene work well as chain-transfer agents with the Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ catalyst and, if the monomer in question is reactive enough (e.g., norbornene), that it is possible to pulse the system with monomer in the presence of the CT agent to give polymers with relatively low polydispersities.

Vinylalkylidene complexes are observable intermediates in reactions in which 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene[5] or acetylene[6b] is polymerized and were found to be relatively stable. A number of simpler vinylalkylidene complexes have subsequently been prepared and isolated by reaction of *cis*- or *trans*-1,3-pentadiene with M(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ or M(CH-*t*-Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$ (M = Mo or W) in the presence of a suitable Lewis base.[8] When less reactive neopentylidene complexes W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ or Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ were treated with 1,3-pentadiene, the initiator was slowly consumed but no new alkylidene complexes were observed. However, living polymers derived from norbornene were found to react rapidly with 1,3-pentadiene to generate vinylalkylidene complexes M(CHCH=CHMe)(NAr)(O-*t*-Bu)$_2$ and capped polymers (eq 1). Although the tungsten vinylalkylidene complex decomposed in C_6D_6 over the course of several hours, the molybdenum complex[9] proved to be stable at a concentration of ~0.01 M for 24 h.

(1)

M = Mo(NAr)(O-t-Bu)$_2$

The observation that living polyenes derived from acetylene are excellent initiators for ROMP[6b] suggested that the in situ generated vinylalkylidene complexes described

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