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RAFT Polymerization of Acrylonitrile and Preparation of Block Copolymers Using 2-Cyanoethyl Dithiobenzoate as the Transfer Agent

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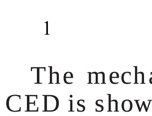
The past decade has witnessed significant developments in the field of controlled/living radical polymerization (CRP),[1−4] which enables one to synthesize polymers with controlled molar mass, narrow molecular weight distribution, and well-defined architectures and functionalities.[5−8] Several CRP processes were investigated in detail, including atom transfer radical polymerization (ATRP) using transition metal complexes,[9−11] nitroxide-mediated polymerization (NMP) using nitroxides,[12] and reversible addition−fragmentation chain transfer (RAFT) using dithioesters.[4,13] CRP is compatible with a wide range of monomers including acrylates, methacrylates, and styrene. Acrylonitrile (AN) is a challenging monomer because of its high reactivity and the poor solubility of polyacrylonitrile (PAN). Nevertheless, PAN is used in several important applications, such as the preparation of carbon fibers,[14] which motivates one to synthesize polyacrylonitrile (PAN) in a controlled way. Our group[15−17] already reported the synthesis of well-defined PAN by ATRP. Furthermore, we investigated the synthesis of block copolymers containing AN and *n*-butyl acrylate (*n*-BA) with well-defined structures,[17] which were needed directly to prepare nanostructured carbon arrays by pyrolysis.[18] Hawker and coworkers,[19] and our group,[17] reported controlled synthesis of PAN using NMP. Block copolymers of AN and *n*-BA were also prepared with well-defined structures by our group.[17]

The preparation of PAN by RAFT has not yet been reported. RAFT involves a reversible addition−fragmentation chain transfer between an active and a dormant species and is performed by adding a suitable dithioester transfer agent (**1**), which has the appropriate Z and R groups selected to provide an effective transfer process.[20−22] Our first attempts to use cumyl dithiobenzoate (CDB, **2**) in AN polymerizations did not control the polymerization well (entries 3 and 4, Table 1). In this paper a new dithioester, 2-cyanoethyl dithiobenzoate (CED, **3**), is introduced as a RAFT agent, allowing preparation of PAN and its block copolymers with narrow molecular weight distribution.



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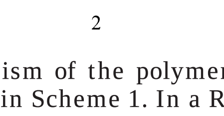

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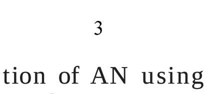

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The mechanism of the polymerization of AN using CED is shown in Scheme 1. In a RAFT polymerization, the choice of both the Z and R groups is extremely important in achieving high chain transfer constants.[21,22] The rate of addition of radicals to dithioester is strongly influenced by the nature of the substituent group Z, which is usually selected to stabilize the intermediate radicals; consequently, the substituents that stabilize these radicals could retard their rate of fragmentation. For example, the polymerization of *n*-BA or vinyl acetate is strongly retarded when performed with cumyl or benzyl dithiobenzoates as the RAFT agent[20,23] because of the slow fragmentation of the intermediate radicals or their reaction with propagating radicals. An earlier study[21] indicated that rates of polymerization of monomers with substituents stabilizing radicals do not markedly depend on the structure of Z. The selection of the R group could be more important in the polymerization of acrylonitrile. R should be a good homolytically leaving radical group that should also efficiently reinitiate polymerization. When using CED for the RAFT polymerization, the expelled $CH_3{-}CH{\cdot}(CN)$ radicals should effectively initiate the polymerization of AN, since they resemble propagating radicals. Indeed, 2-bromopropionitrile, which generates such radicals, was successfully used for the synthesis of PAN using ATRP.[15−17]

Polymerizations of AN were conducted with two different ratios of initiator and RAFT agent at 60 °C (for experimental conditions cf. the Supporting Information). The results are shown in Table 1. When a ratio of initiator to RAFT agent of 1:10 was used in the polymerization, the gel permeation chromatography (GPC) traces are bimodal, although the overall polydispersity is only 1.29 (entry 1, Table 1). Increasing the concentration of initiator (entry 2, Table 1) produced preparation of a polymer with a narrow molecular weight distribution throughout the reaction ($M_w/M_n = 1.05{-}1.14$) while achieving 40.2% conversion in 7 h (Figure 2).

Figure 1 (sample refers to entry 2 in Table 1) is the ^1H NMR spectrum of PAN prepared by the RAFT process with CED as transfer agent. Peaks at 1.2−1.6 and 7−8 ppm correspond to CH_3 and aromatic protons from the RAFT transfer agent CED, respectively. The molecular weight of PAN was calculated by comparison of the area of peak corresponding to polymer backbone CH_2 protons to those corresponding to CH_3 protons from the end groups.

The molecular weight determined from ^1H NMR increased linearly with conversion as shown in Figure 2. The experimental values deviated only slightly from the theoretical values. The molecular weight shifted cleanly to higher values with preserved low polydispersities; some tailing is noticed. (cf. Supporting Information).

The polymerization of AN was also conducted using CDB as RAFT agent to compare the effect of different R groups, cumyl and 2-cyanoethyl, on the control of polymerization. However, in the case of CDB, the polymerization could not be controlled by using various ratios of AIBN and CDB, as shown in Table 1 (entries 3 and 4, Table 1). With a low concentration ratio of initiator to transfer agent, the polymerization was strongly retarded. However, at a high value of this ratio, the resulting polymer exhibited a multimodal distribution of molecular weights and a polydispersity as high as 2.0, similar to the free radical polymerization of acrylonitrile initiated by AIBN. Thus, either the cumyl

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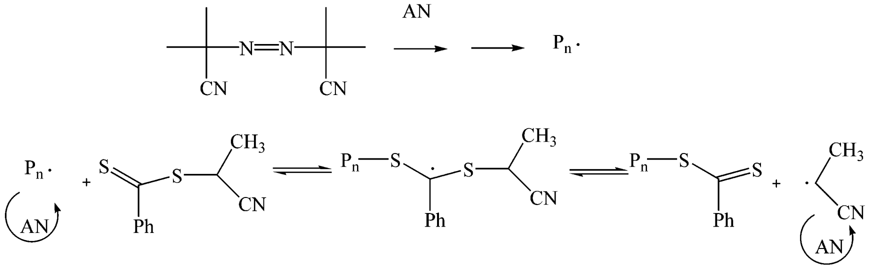
Table 1. Homopolymerization of AN and Chain Extension Using PAN or PBA as Macroinitiator in Ethylene Carbonate at 60 °C

<table>
<tr><th>Entries</th><th>RAFT Agent[a]</th><th>Monomer A[b]</th><th>[M]/[AIBN] /[RAFT Agent]</th><th>M_n^c (GPC)</th><th>M_n (NMR)</th><th>M_w/M_n (GPC)</th><th>Time (h)</th><th colspan="3">Conversion (%)</th></tr>
<tr><td>1</td><td>CED</td><td>AN</td><td>2000/1/10</td><td>12500</td><td>2500</td><td>1.29</td><td>67</td><td colspan="3">25.0</td></tr>
<tr><td>2</td><td>CED</td><td>AN</td><td>500/1/3</td><td>15500</td><td>4000</td><td>1.05</td><td>7</td><td colspan="3">40.2</td></tr>
<tr><td>3</td><td>CDB</td><td>AN</td><td>2000/1/10</td><td>1800</td><td><500</td><td>1.06</td><td>186</td><td colspan="3"><5</td></tr>
<tr><td>4</td><td>CDB</td><td>AN</td><td>1800/1/5</td><td>16400</td><td>4900</td><td>2.08</td><td>15</td><td colspan="3">38.8</td></tr>
<tr><td colspan="7"></td><td>Monomer B[b]</td><td>[M]/[AIBN]/ [Macroinitiator]</td><td>M_n^c (GPC)</td><td>M_w/M_n (GPC)</td></tr>
<tr><td>5</td><td>CED</td><td>AN</td><td>500/1/3</td><td>5500</td><td>1300</td><td>1.15</td><td>*n*-BA[d]</td><td>900/1/10</td><td>7800</td><td>1.17</td></tr>
<tr><td>6</td><td>CDB</td><td>*n*-BA</td><td>7812/1/10</td><td>54900</td><td>/</td><td>1.15</td><td>AN[e]</td><td>9000/1/10</td><td>54400</td><td>2.02</td></tr>
<tr><td>7</td><td>CDB</td><td>*n*-BA</td><td>500/1/10</td><td>3500</td><td>/</td><td>1.12</td><td>AN[e]</td><td>1000/1/10</td><td>4900</td><td>1.81</td></tr>
</table>

[a] CED = 2-cyanoethyl dithiobenzoate, CDB = cumyl dithiobenzoate. [b] AN = acrylonitrile, *n*-BA = *n*-butyl acrylate. [c] Molecular weight value measured by GPC gives higher values than the true values, as reported previously.[17] [d] For monomer B = *n*-BA, macroinitiator = PAN. [e] For monomer B = AN, macroinitiator = PBA.

Scheme 1. Mechanism of Homopolymerization of AN (Acrylonitrile) by RAFT Polymerization



radical is much more stable than the 2-cyanoethyl radical and reinitiates polymerization of AN very slowly or the fragmentation of the cumyl group from the adduct is slow, which leads to retardation.

The dithiobenzoate-terminated PAN obtained from the polymerization using CED as RAFT agent was employed as a macroinitiator for chain extension with *n*-BA by RAFT process (entry 5, Table 1). We used a low-molecular-weight PAN in order to achieve a homogeneous reaction system as described in our previous study.[17] To achieve high blocking efficiency, the first dithiobenzoate-terminated block should have a high transfer constant in the subsequent polymerization of second monomers.[24,25] This requires that the first polymer should have an R group with a leaving ability greater than, or at least comparable to, that of the second polymer radical. Therefore, PAN should be chain extended with *n*-BA, since acrylonitrile-propagating radicals are “better” leaving groups than acrylic ones. Under such circumstances, molecular weight shifts cleanly to the higher range, with polydispersity remaining below 1.20 (cf. Supporting Information). This demonstrates that the chain extension from PAN to *n*-BA can be well controlled and provides block copolymers with narrow molecular weight distribution.

Chain extension from poly(*n*-butyl acrylate) (PBA) to AN was also attempted to compare the blocking efficiency of the reverse chain extension with the successful chain extension described above (entries 6 and 7, Table 1). Well-defined dithiobenzoate-terminated PBA, with high and low molecular weight, was synthesized and then chain extended with acrylonitrile. The GPC traces of the resulting copolymers were multimodal with high polydispersity throughout the reaction, which indicates a low blocking efficiency. These experiments confirm the results obtained earlier with ATRP and NMP,[17] that PAN macroinitiators can more easily cross-propagate and polymerize *n*-BA (the second block) than the reverse chain extension reaction from PBA to AN.

In conclusion, a novel RAFT agent CED is efficient for the preparation of PAN with low polydispersity and controlled molecular weight. These PAN polymers can

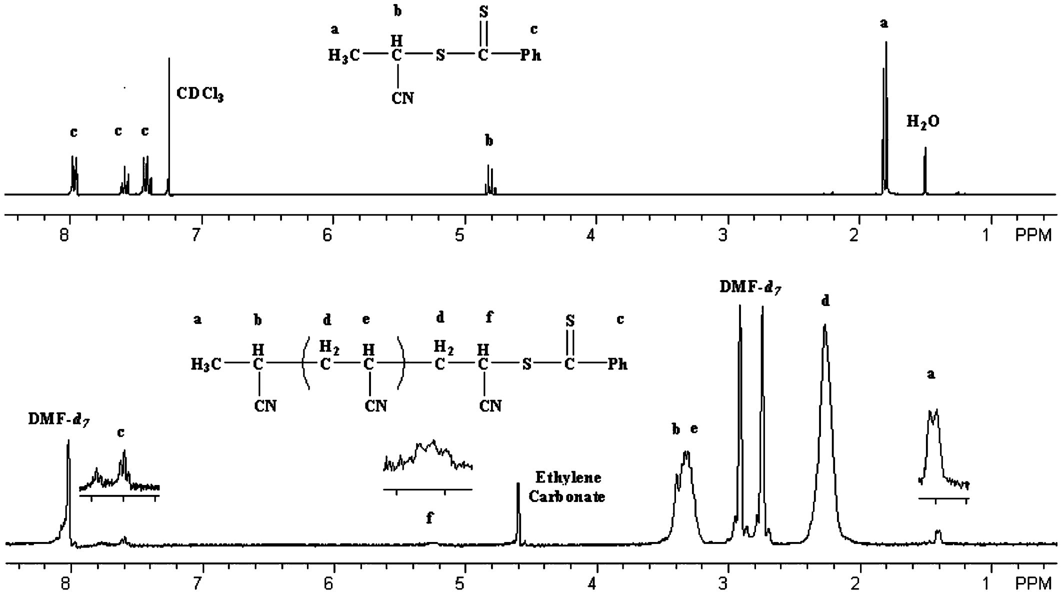


Figure 1. 300 MHz ^{1}H NMR spectrum of dithiobenzoate-terminated PAN prepared by RAFT with CED.

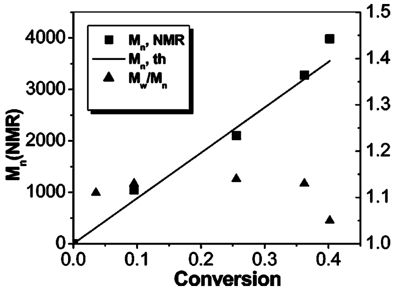


Figure 2. Number-average molecular weight and polydispersity as a function of conversion for polymerization of AN by RAFT using CED as a transfer agent in ethylene carbonate at 60 °C. [AN] = 4.54 M, [AN]/[AIBN]/[CED] = 500/1/3.

be successfully used to prepare PAN-*b*-PBA block copolymers by chain extension from PAN to *n*-BA. Further improvement in the design of RAFT agents for AN polymerization is needed for lower polydispersity and higher molecular weight of (co)polymers.

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Supporting Information Available: Details of synthesis of RAFT agent; homopolymers and block copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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