Polymer Bulletin 52, 17–23 (2004)
DOI 10.1007/s00289-004-0244-6

Polymer Bulletin

A New Azo Initiator for the Synthesis of Polymers with Pyrene Terminal Groups

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Received: 24 October 2003/Revised version: 15 March 2004/ Accepted: 25 March 2004

Summary

4,4'-azobis(4-cyanopyrenylmethyl pentanoate) (ACPMP) was synthesized by the reaction of pyrenylmethanol with 4,4'-azobis(4-cyanopentanoyl chloride) (ACPC). ACPMP was further used in the synthesis of polystyrene with pyrene terminal groups by using conventional free radical polymerization (FRP) and stable free radical polymerization (SFRP) techniques. Incorporation of terminal groups were confirmed by spectral measurements.

Introduction

Telechelic polymers are defined as macromolecules that contain functional end groups [1]. A number of techniques for the preparation of polymers with desired end groups have been developed. Besides controlled/living polymerization techniques, functional initiator approach in conventional free radical polymerization is widely used because of its simplicity and applicability to a great number of monomers. In order to obtain functional polymers, the initiating compound has to be at least bifunctional - it must carry one or more functional site other than the thermolabile group [2]. Due to the potential variability in the chemical nature of the azo initiators it is possible to prepare telechelics with a wide variety of functional groups. Previously, hydroxyl [3-7], carboxylic acid [8, 9], carboxylic acid chloride [10], ester [11], azide [12], isocynate [12], nitril [11, 13], trichloromethyl [14], *N,N*-dimethyl amino [15], acyloximino [16], dibenzazepine [17], benzoin [18], furanyl [19] and tiophene-functional [20] azoinitiators were used to yield the corresponding telechelics.

Pyrene containing polymers have attracted much attention due to their potantional use as semiconductors, photoresist materials and fluorescent probes [21]. Various methods have been developed to attach pyrene moieties to polymers. For instance, living anionic [22-24] and Atom Transfer Radical Polymerization (ATRP) [25, 26] processes were successfully applied to prepare polymers with pyrene termini.

In this article, we report the synthesis of an azo-pyrene initiator (ACPMP) having appropriate functionality for subsequent vinyl polymerization to yield pyrene terminated polymers.

Experimental

Materials

4,4'-azobis(4-cyanopentanoyl chloride) (ACPC) was prepared according to a previously described procedure [27]. Styrene (St) was purified by the usual methods and distilled in vacuo over CaH2. Tetrahydrofuran (THF) was purified by refluxing with KOH and fractionally distilling from sodium and stored above CaH2. Pyrenylmethanol, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and triethylamine (Aldrich) were used as received.

Synthesis of 4,4'- azobis(4-cyanopyrenylmethyl pentanate) (ACPMP)

A solution of 0.49 g (2.13 mmol) of pyrenylmethanol in 20 mL of THF was added dropwise with stirring to a solution of 0.34 g (1.07 mmol) of ACPC and 3 mL (21.3 mmol) of triethylamine in 20 mL of THF under nitrogen atmosphere at 0 °C. After 24 h, the reaction mixture was passed through a column of basic silica gel to remove the salt. THF was removed by evaporating and the residue was dried in a vacuum oven. Yield: % 20, m.p.: 116 °C.
Elemental analysis : $C_{46}H_{36}N_4O_4$ (708) Calc. C 77.9; H 5.12, Found: C 78.3; H 5.39

Free Radical Polymerization by using ACPMP

(a) Conventional Free Radical Polymerization (FRP)
Styrene and ACPMP as an initiator, in a pyrex tube, were degassed and sealed under nitrogen. The tube was than placed in a thermostatically controlled bath at 65 °C. After a 4h, polymerization mixture was diluted with THF and poured into methanol. The solid was collected after filtration and dried in a vacuum oven.

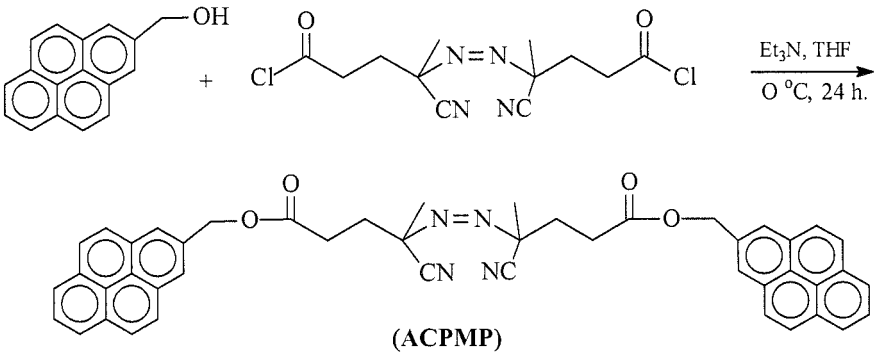
(b) Stable Free Radical Mediated Polymerization (SFRP)
Styrene, in a pyrex tube, containing ACPMP as an initiator and excess TEMPO was deaerated by bubling with nitrogen and subsequently placed in an oil bath. Polymerization was carried out at 130 °C for 5 hours. At the end of the polymerization time, the mixture was diluted with THF and precipitated in methanol. The solid was collected after filtration and dried in a vacuum oven.

Analyses

The FTIR spectrum was taken by the KBr pelletization method using a Jasco 5300 spectrometer. Molecular weight and molecular weight distribution of the polymers were determined by gel permeation chromatography (GPC) on a Waters instrument equipped with R410 differential refractometer and 600E pump using polystyrene standards. THF was used as the eluent at a flow rate of 1.0 mL/min. ^{1}H-NMR measurements were performed in $CDCl_3$ solution using a Bruker 250 MHz instrument. Steady state fluorescence (SSF) measurements were carried out using Perkin Elmer Model LS-50 Spectrofluorimeter. All measurements were made at 90° position and slit widths were kept 10 nm.

Results and Discussion

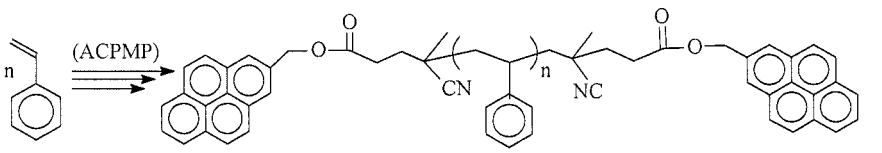
The azo-pyrene initiator (ACPMP) was synthesized by reacting the 4,4'-azobis(4-cyanopentanoyl chloride) with pyrenylmethanol according to the following reaction.



(ACPMP)

The structure of the new azo-pyrene initiator was confirmed by elemental analysis as well as spectroscopic investigations. The FTIR spectrum contains the characteristic ester, aliphatic and aromatic bands at 1590, 1730 and 2900 cm^{-1}, respectively (Figure 1). The ^{1}H-NMR specrum recorded in $CDCl_3$ evidenced resonance signals of the phenyl and CH_2 protons of relative intensities (Figure 2 a).

Styrene was used as a representative monomer to test the efficiency of the azo-pyrene initiator for free radical polymerization. A typical polymerization of bulk styrene with ACPMP (5×10^{-3} M) at 65 °C produced 5 % of polystyrene ($M_n = 18 \times 10^4$, M_w/M_n = 1.9) after 4h. A control experiment without the azo-pyrene initiator produced negligable amount polymer at the same reaction time. In conventional free radical polymerization, the number of functionality of the polymer depends greatly on the kinetic behavior of the particular monomer involved. Initiation of styrene polymerization by means of radical initiator ACPMP is expected to yield pyrene moiety at both end because of the radical-radical combination type termination (equation 2).



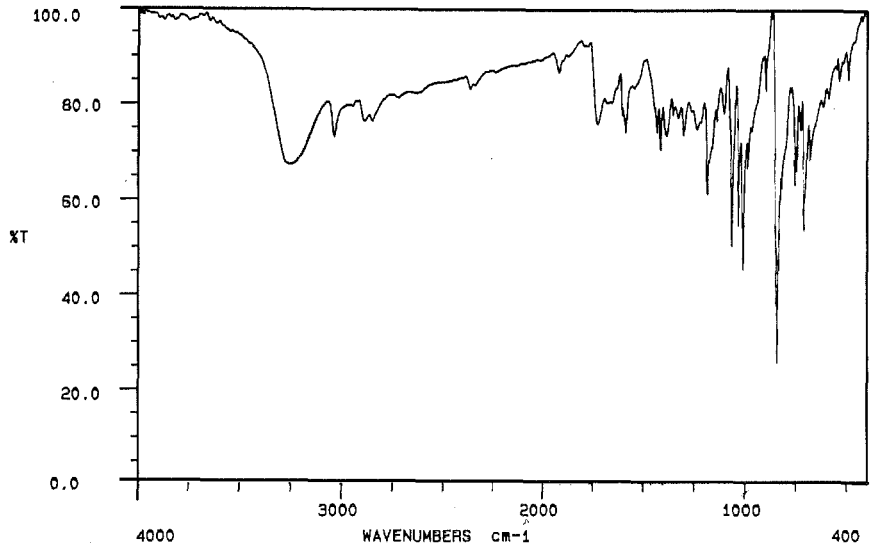
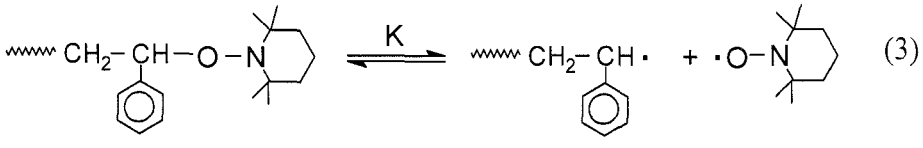


Figure 1. IR spectrum of the azo-pyrene initiator, ACPMP, in KBr.

Accurate control of polymerization process is an important aspect for the preparation of well-defined end-functionalized macromolecules. Recent developments in controlled/living radical polymerization [28] provided possibility to synthesize well-defined telechelic polymers with controlled functionality via ATRP, Stable Free Radical Mediated Polymerization (SFRP), and Reversible Addition-Fragmentation Chain Transfer Polymerization (RAFT). For our purpose, it seemed appropriate to use SFRP procedure since functional free radical initiators can be employed in conjunction with a stable radical and it tolerates a wide variety of functional groups [29].

SFRP can be realized through reversible deactivation of growing radicals by a stable radical such as 2, 2, 6, 6-tetramethyl-1-piperidinyloxy (TEMPO).



(3)

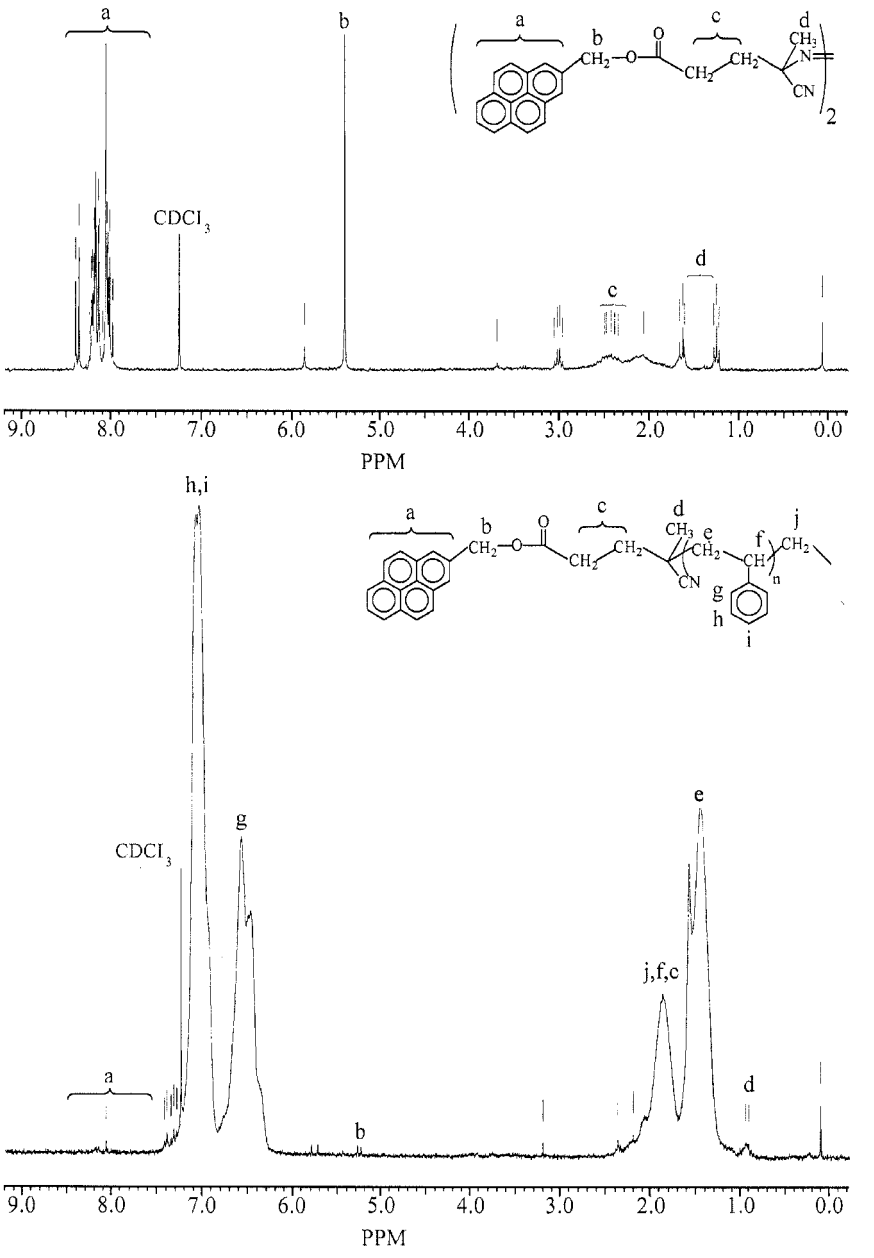


Figure 2. ^{1}H-NMR spectra of ACPMP (a) and pyrene-terminated polystyrene (b) in $CDCl_3$.

SFRP of St in bulk by using ACPMP (5 x10^{-3} mol l^{-1}) in the presence of excess TEMPO (15 x 10^{-3} mol l^{-1}) at 130 °C for 5 h. yielded polystyrene with 20 % conversion and molecular weight of M_n = 19 x 10^3. The narrow molecular weight distribution (M_w/M_n = 1.13) indicates that the polymerization is well controlled.

Obviously, this process leads to the formation of monofunctional polymers since the other chain end always contains TEMPO moiety due to the fast deactivation process characteristic to the SFRP [29]. The polymer structure was assigned by means of H-NMR and fluorescence spectral measurements. As can be seen from Figure 2b, the H-NMR spectrum of the above obtained polymer contains aromatic protons of pyrene moiety at 7.9-8.2 ppm in addition to usual polystyrene aromatic protons.

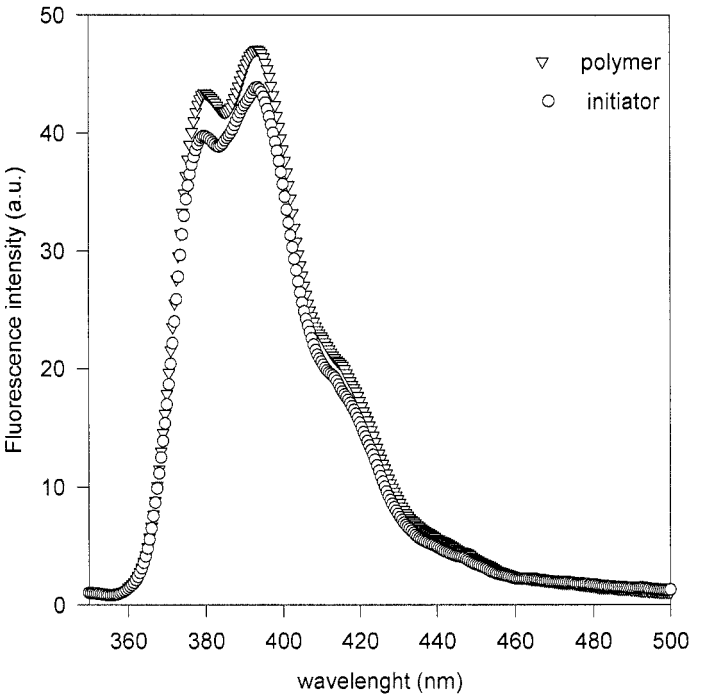


Figure 3 Fluoroscence spectra of ACPMP and pyrene-terminated polystyrene in CH_2Cl_2, $\lambda_{exc.}$ = 350 nm.

Figure 3 shows the fluorescence emission spectra of ACPMP and the polymer obtained therefrom in toluene at room temperature. The spectrum of the polymer shows the vibrational structures of the pyrene chromophore. These spectroscopic investigations suggest that pyrene groups were successfully incorporated into the polymer chain.

Although these results are preliminary in nature, they serve to indicate the efficiency and convenience of using pyrene-azo initiator to introduce pyrene units to polymer chain ends. Such processes would have considerable value in studying polymer-polymer adsorption and random coil structures. Further studies in this line are now in progress.

Acknowledgements

The authors would like to thank Istanbul Technical University, Research Fund for financial support. Y.Y. thanks Turkish Academy of Science for its generous support.

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