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Communications to the Editor

Photoinduced Synthesis of Amino-Functional Telechelics

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In recent years, the synthesis of prepolymers having deliberately introduced reactive end groups[1−5] (telechelics) has become an attractive field of polymer science because of their utilization as cross-linker, chain extender, and precursors for block and graft copolymers. Moreover, star and dendritic polymers are obtained by coupling reactions of monofunctional and multifunctional telechelics with appropriate reagents. As generally accepted, termination in living polymerization is the most convenient way to prepare telechelics with well-functionalized and predetermined structures. In addition to well-established living anionic polymerization, several new polymerization systems have been developed[6,7] during the last years which allowed preparation of telechelics following the common strategy.

An alternative to living polymerization, and a very often used pathway to introduce functional groups to polymers, is the use of bifunctional initiatiors in free-radical polymerization (Scheme 1). A variety of bifunctional initiators with carboxyl, hydroxyl, nitrile, and isocyanate groups have been used[8−11] for this purpose.

A functional initiator approach to synthesize amino telechelics causes some complications since amino compounds participate in chain-transfer reactions.

Recently, Song et al.[12] reported that pendant amino groups can be introduced effectively when polymers bearing (acyloxy)imino groups irradiated in the presence of benzophenone followed by hydrolysis (Scheme 2). In this paper, we report a convenient and simple synthetic method for the preparation of amino telechelics via free-radical polymerization using (acyloxy)imino azoinitiator (AOAI) and subsequent photolysis and hydrolysis.

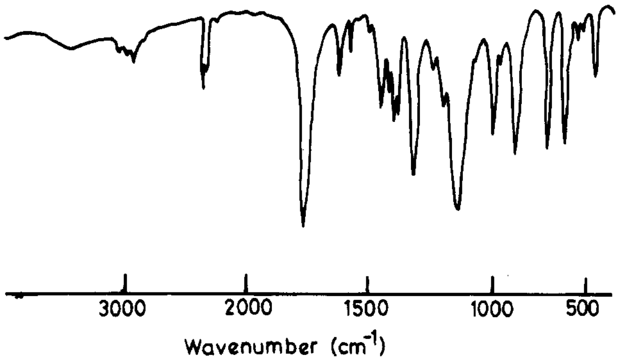

Figure 1. IR spectrum of AOAI.

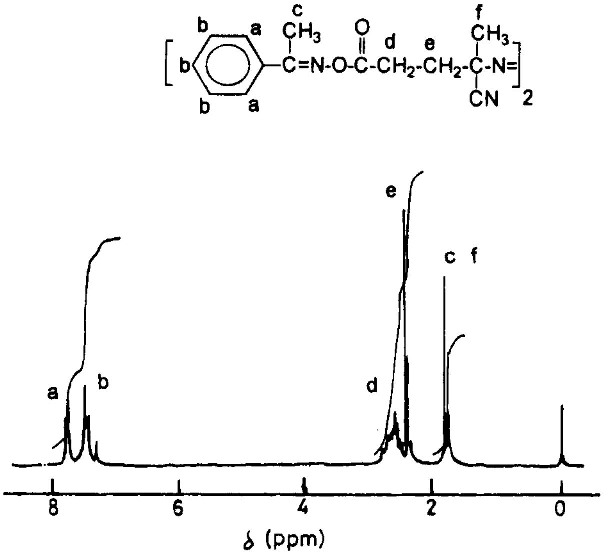

Figure 2. ^{1}H-NMR spectrum of AOAI.

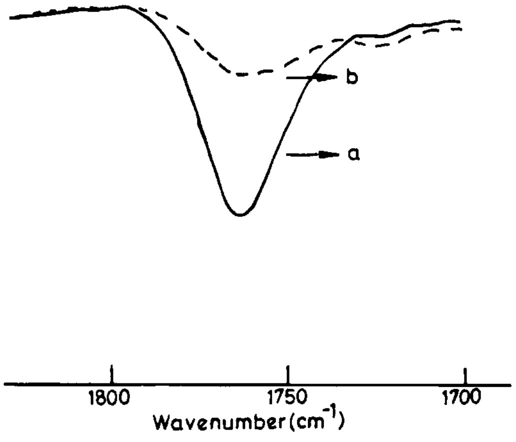

Figure 3. IR spectra of amino-terminated polystyrene (a) before and (b) after irradiation.

AOAI was synthesized by reaction of acetophenone oxime with 4,4′-azobis(4-cyanopentanoyl)dichloride as shown by Scheme 3. The structure of the new AOAI initiator was confirmed by elemental analysis as well as spectroscopic investigations. The IR spectrum contains the characteristic C=O and C=N bands at 1760 and 1620 cm^{-1}, respectively (Figure 1). The ^{1}H-NMR spectrum, recorded in $CDCl_3$, evidenced resonance signals of 1.7 (CH_3), 2.4 (CH_2), 2.48 (CH_3), and 7.4−7.88 (monosubstituted benzene ring protons) of relative intensities corresponding to the number and type of protons (Figure 2). AOAI was used as a free-radical initiator for the polymerization of styrene in DMF. In a typical experiment, thermolysis of a styrene solution (6.5 mol/L) containing 4.25×10^{-5} mol/L of AOAI at 70 °C yielded polystyrene with 48% yield and 39 000 molecular weight as determined by GPC. The initiation of polymerization by means of AOAI yields polymers with one or two groups according to the termination mode of the particular monomer involved. The following reactions (Scheme 4) may be written for styrene polymerization since styrene-derived radicals terminate almost exclusively by combination. The anticipated benzophenone-sensitized photoreaction of polymer bearing

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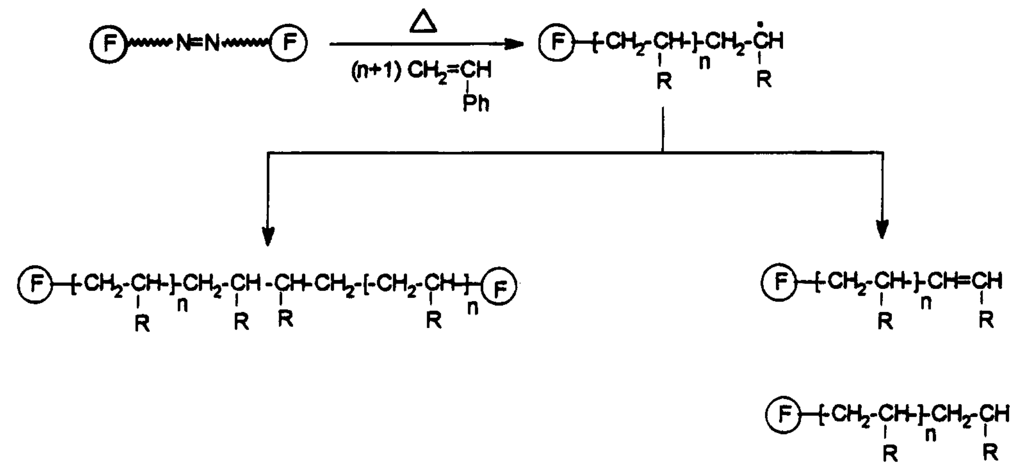
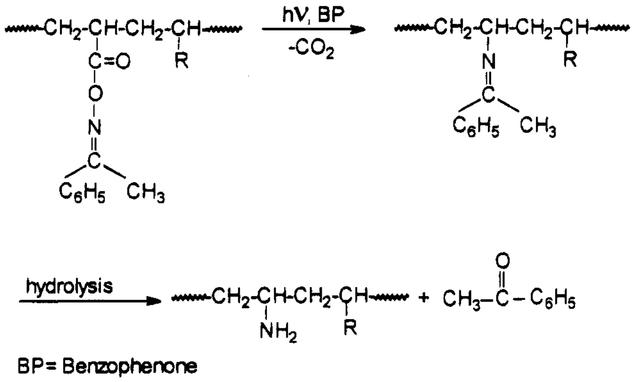
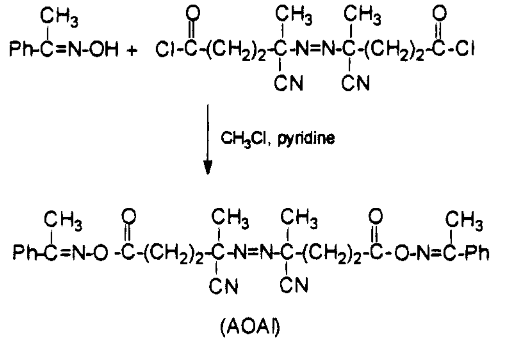
Scheme 1



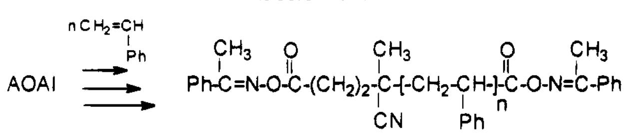
Scheme 2



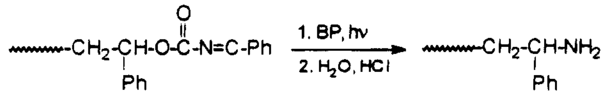
Scheme 3



Scheme 4

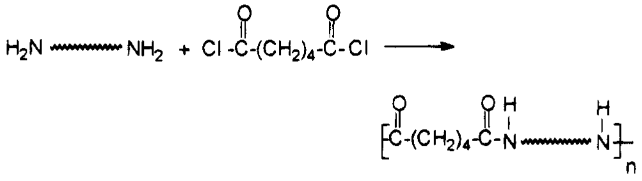


Scheme 5



(acyloxy)imino groups is shown in Scheme 5. Decomposition of AOI groups was followed by the change in absorbance at 1765 cm^{-1} in the IR spectra of the polymer before and after irradiation (Figure 3). Polymers were then treated with a dilute aqueous solution of HCl to transform α-methylbenzylidene imino groups into amino groups. The obtained amino-terminated telechelics were subjected to chain extension with adipoyl chloride in methylene chloride as described in the Experimental Section and gave positive evidence for the ability of amino chain ends to participate in polyamidation (Scheme 6). The polyamidation reaction caused a 157% increase in the molecular weight of the initial polymer (M_n = 91 000). The infrared spectrum of the obtained polymer exhibits bands at 3400 (N−H stretching), 1650 (C=O stretching), and 1600 cm^{-1} (N−H bending) in addition to the usual absorption bands of polystyrene (Figure 4).

Scheme 6



Although these results are preliminary in nature, they serve to indicate the efficiency and convenience of AOAI to introduce amino chain ends into polymers. Further studies are now in progress.

Experimental Section. Materials. Styrene and solvents were purified by conventional drying and distillation procedures. Acetophenone oxime[13] and 4,4′-azobis(4-cyanopentanoyl)dichloride[14] (ACPC) were prepared as described previously.

Synthesis of Azoacetophenone Oxime Ester Initiator (AOAI). In a three-necked flask fitted with a stirrer were introduced 1.54 g (11.4 mmol) of acetophenone oxime and 50 mL of dry chloroform, and the mixture was treated with 1 mL of dry pyridine. The solution was stirred at 0 °C, while 1.8201 g (5.7 mmol) of ACPC dissolved in 25 mL of chloroform was added dropwise under nitrogen. The mixture was stirred for another 3 h at this temperature and allowed to stand overnight. The solution was washed with water and dried over $CaCl_2$, and the initiator was then precipitated in excess *n*-hexane, giving white crystals of AOAI in a yield of 70%: mp 115−120 °C. Elem. anal. Calcd: C, 65.24; H, 5.82; N, 16.31. Found: C, 65.06; H, 5.01; N, 16.67.

Polymerization Procedures. An appropriate solution of styrene (6.5 M) in dimethylformamide containing a known amount of azooxime ester initiator (4.25 × 10^{-5} M) was degassed with nitrogen and placed in a thermostat at 70 °C. At the end of the polymerization, the reaction mixture was poured into a 10-fold excess of methanol, and precipitated polymer was filtered and dried.

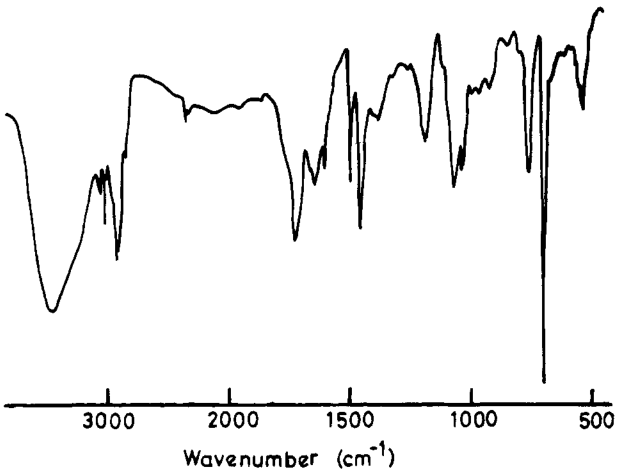


Figure 4. IR spectrum of amino-terminated polystyrene.

Polyamidation. A total of 0.2 g of polymer was dissolved in 4 mL of dichloromethane, 2 drops of pyridine was added to the mixture at room temperature, and an excess amount of adipoyl chloride was added. The mixture was then stirred overnight, and white precipitate was separated by filtration. The remaining solution was precipitated by pouring into methanol and filtered. Finally the polymer was washed with water and methanol and dried.

Photoirradiation. A dichloromethane solution of photoactive polystyrene containing 5 wt % benzophenone (BP) as a sensitizer was irradiated at 366 nm for 10 min by using an Amco monochromatic light source with an Osram XBO 75-W xenon lamp. The decomposition of (acyloxy)imino (AOI) groups was observed by following the change in absorbance at 1760 cm^{-1} in the IR spectra of polymers before and after irradiation. Irradiated polymers were treated with an aqueous solution of 1.2 N HCl by stirring for 1 h and then precipitated in methanol and dried.

Analysis. A ^{1}H-NMR spectrum was recorded on a Varian Gem 200 spectrometer in the pulsed Fourier transform (FT) mode using TMS as an internal standard. IR spectra were recorded on a Jasco FT-IR 5300 spectrometer. Elemental analysis was carried out with a Yanaco-CHN MT3 type instrument. Molecular weights of polymers were calculated from GPC chromatograms according to standard polystyrene samples using a Knauer M-64 type instrument and THF as the eluent at a flow rate of 1 mL/min.

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References and Notes

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