SYNTHESIS OF ACRYLONITRILE COPOLYMERS BY ATOM TRANSFER RADICAL POLYMERIZATION AND NMR STUDIES

by

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The work embodied in this thesis has not been submitted, in part or full, to any other University or Institute for the award of any degree or diploma.

31/5/06

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Dedicated

To

My Family

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Abstract

The acrylonitrile copolymers, being the materials of significant commercial importance, have attracted much attention in academics and industry. The synthesis of these copolymers has been accomplished through conventional free radical polymerization, which does not allow any precise control over molecular parameters and structure. The advent of Controlled Radical Polymerization (CRP) has minimized these drawbacks by showing advantage in terms of control over the molecular weight distribution, the copolymer composition, the architecture, and the functionality of polymer, thus making it more industry-friendly.

Atom Transfer Radical Polymerization (ATRP) is one of the versatile techniques of CRP which is based on a reversible exchange between a low concentration of growing radicals and a dormant species; this dynamic equilibrium keeps control over the termination as well as side reactions leading to the uniform growth of polymer chains throughout the polymerization.

Since 1995 ATRP has emerged as an effective technique for the controlled polymerization of wide range of monomers. Irrespective of the number and type of monomers, which can be successfully polymerized, ATRP has also been shown to be more versatile with respect to the synthesis of novel architectures like gradient, graft, block, and star copolymers.

In ATRP, the variation in relative concentration of monomers is reflected along all the chains, and the distribution of monomer units influences the physical properties of polymers to a great extent. Hence, the knowledge about the

composition and distribution of monomer units along the macromolecular chains is important to correlate the structure-property relationship.

High-resolution NMR spectroscopy has proven to be one of the most informative techniques for the microstructure analysis. NMR spectroscopy plays an important role in monitoring the extent of reaction, checking the purity of polymer samples along with their identification. Various 2D NMR techniques in conjugation with 1D NMR techniques helps in the detection of end groups and in determining the tacticity of polymers synthesized by ATRP and thus helps in the understanding of polymerization mechanism involved.

The thesis consists of six chapters. ***Chapter 1*** deals with the literature survey on the current advances in the field of "Atom Transfer Radical Polymerization" and "NMR of Polymers". This chapter signifies the importance of the research project undertaken in the field of polymer chemistry. A general introduction to ATRP regarding its mechanism and kinetic studies is covered. The use of various initiators and catalyst systems for the controlled polymerization of wide range of monomers under ATRP conditions has been reviewed. The importance of NMR spectroscopy in analyzing the sequence distribution of polymers and their characterization is also incorporated. The approach applied for the current research, and its contribution to the field of NMR and polymers is also highlighted.

Chapter 2 contains the experimental details for the optimization and standardization of homopolymerizations, copolymerizations and block copolymerizations by ATRP using different initiators and catalyst systems. The experimental details for the 1D (^{1}H, $^{13}C\{^{1}H\}$, DEPT-45, 90, 135) and 2D

(heteronuclear single quantum correlation (HSQC), total correlated spectroscopy (TOCSY), and heteronuclear multiple bond correlation (HMBC)) NMR experiments are incorporated. The details of calculation of theoretical and experimental molecular weights, outfeed compositions, and the calculation of resonance signal intensities are also included in this chapter. The theoretical basis and experimental details about the optimization of the reactivity ratios from the infeed/outfeed fractions using the least square methodology are also given.

Chapter 3 deals with the copolymerization of acrylonitrile (A) and ethyl methacrylate (E) using copper based ATRP at ambient temperature (30°C) using various initiators. High monomer conversions within reasonable time were desired while maintaining control over molecular weight distribution. The effect of various reaction parameters on the rate of polymerization, like the variation in temperature, $[ligand]_0/[catalyst]_0$ ratio, initiator concentration, catalyst concentration, and type of initiator and ligand used for ATRP were examined, to achieve controlled polymerizations. A series of the A/E copolymers with varying infeed molar ratios were synthesized in bulk at ambient temperature (30°C) using CuBr/bpy catalyst and BPN as initiator with optimized molar ratio $[Monomers]_0$: $[BPN]_0$: $[CuBr]_0$: $[bpy]_0$ = 200: 1: 0.5: 1.5.

The controlled nature of polymerization was demonstrated by linear evolution of molecular weights with conversion while maintaining low polydispersities [$1.1<(M_w/M_n)<1.4$]. The living nature of polymerization was further confirmed by performing the kinetic study. The high chain-end functionality of the A/E copolymers was confirmed by successful block

copolymerization with methyl acrylate and styrene. The monomodal nature of GPC curves confirmed the formation of block copolymers.

The copolymer composition obtained from ^1H NMR spectra were utilized to determine the monomer reactivity ratios (r_A = 0.68 and r_E = 1.75) involved in ATRP. 2D NMR (HSQC and TOCSY) experiments were employed to resolve the highly overlapping and complex ^1H and $^{13}C\{^1H\}$ NMR spectra of A/E copolymers. 2D HSQC and TOCSY spectral analysis facilitate the assignments of the backbone methylene carbon resonances up to the tetrad level. The α-methyl and methine carbon resonances were assigned up to pentad level. Unambiguous spectral assignments for the complex and overlapped carbonyl and nitrile carbon regions were done with the help of 2D HMBC NMR spectral studies. The important role of 2D HSQC and TOCSY experiments in conjunction with 2D HMBC NMR experiments for the microstructure analysis of copolymers is described.

Chapter 4 contains the optimization of reaction conditions for the ATRP of acrylonitrile/n-butyl acrylate (A/B) and acrylonitrile/2-methoxy ethyl acrylate (A/M) with different initiator and catalyst. 2-bromopropionitrile (BPN) was used as the initiator with CuCl/2,2′-bipyridine (bpy) catalyst system at 60°C. Variation of feed composition led to copolymers with different compositions. ^1H NMR was employed to determine the copolymer composition. The reactivity ratios determined with the methodology based on Mao-Huglin terminal model (r_A = 1.30 and r_B = 0.68 for A/B copolymers; r_A = 1.52 and r_M = 0.60 for A/M copolymers) were found to be in good agreement with those known for conventional radical polymerization. The molecular weight distribution data, determined by gel

permeation chromatography (GPC) showed a linear variation with conversion indicating towards the controlled nature of polymerization.

With the help of $^{13}C\{^{1}H\}$ and DEPT NMR, the distinction between various carbon resonance signals (methyl, methylene, methine and quaternary carbons) was done. The overlapping and broad signals of copolymers were assigned completely to various compositional and configurational sequences by correlating 1D (^{1}H, $^{13}C\{^{1}H\}$, DEPT) and 2D (HSQC, TOCSY, HMBC) NMR spectral data.

The configurational and compositional sensitivity of quaternary carbons, viz. carbonyl and nitrile carbon regions was investigated through the analysis of long range couplings between carbon and protons with the help of 2D HMBC NMR experiments. The completely assigned ^{1}H NMR spectra was utilized to make assignments in 2D HMBC spectra, which further verify the assignments made using 2D HSQC and TOCSY spectral analysis.

In ***Chapter 5***, the synthesis of block copolymers of acrylonitrile with 2-methoxy ethyl acrylate and ethyl methacrylate under ATRP conditions is described. Block copolymers containing pure polyacrylonitrile segments are not only challenging synthetically, but also interesting because of the morphological and mechanical properties expected from these block copolymers. Initially the ATRP conditions were optimized for the synthesis of macroinitiators of desired molecular weights and narrow polydispersities.

Furthermore, block copolymerization with acrylonitrile was done using macroinitiators of different molecular weights using CuCl/bpy catalyst at 70°C in ethylene carbonate as solvent. The purity of block copolymer was determined by gel permeation chromatography (GPC). The blocking efficiency of the

macroinitiators was investigated using the kinetics as well as molecular weight distribution data. The monomodal nature of GPC curves obtained for these block copolymers confirmed the synthesis of well-defined block copolymers.

The composition of individual blocks in PEGMEA-*b*-PAN copolymers was determined using ^{1}H NMR spectra. The comparison of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of the block copolymers with the homopolymers was also done. P_m, calculated using $^{13}C\{^{1}H\}$ NMR for both the homopolymers and for block copolymer was found to be comparable indicating that the tacticity of the block copolymers matched with those of the homopolymers.

In ***Chapter 6***, the detailed study of copolymerization of acrylonitrile with allyl butyl ether, using ATRP technique is presented. The optimization of various reaction conditions was done in order to achieve copolymers of predetermined molecular weight and narrow molecular weight distribution. Using 2-bromopropionitrile as initiator and CuBr/bpy catalyst, well-defined copolymers having about 30 mol% allyl butyl ether were obtained. Under bulk conditions, the polymerization was well-controlled as evident from the molecular weight distribution data. However, $M_{n,GPC}$ values were slightly higher than $M_{n,th}$ for conversions beyond 45% low conversions. For conversions beyond 45%, the reaction mixture became heterogeneous probably due to the insolubility of deactivating species. Consequently, different solvents were employed to increase and maintain the homogeneity of the solution. The solution polymerization provide better control than the bulk copolymerization, however, the heterogeneity was not completely eliminated. Narrow molecular weight distribution was obtained for polymerization in toluene; suggested conventional ATRP behavior.

Increasing the fraction of allyl butyl ether in the monomer feed led to an increase in the level of incorporation of allyl butyl ether in the copolymer at the expense of the overall conversion. The copolymer composition determined from ^{1}H NMR spectra, were utilized to determine the reactivity ratios (r_A = 6.01 and r_C = 0.10), which reflect the lower reactivity of allyl butyl ether for the copolymerization with acrylonitrile. The complex and overlapping ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra was resolved completely using 2D HSQC NMR spectra. ATRP resulted in a significant incorporation of allyl butyl ether within the copolymer chains along with excellent control of the polymerizations; this fact clearly indicates that allyl butyl ether acted as a comonomer rather than a chain-transfer agent under the employed reaction conditions.

Table of Contents