“Gradient” Polymer Prepared by Complex-Radical Terpolymerization of Styrene, Maleic Anhydride, and *N*-Vinyl Pyrrolidone via γ-Ray Irradiation by Use of a RAFT Process: Synthesis, Mechanism, and Characterization

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Received September 13, 2005; Revised Manuscript Received December 28, 2005

ABSTRACT: A novel “gradient” polymer, prepared by complex-radical terpolymerization of styrene (St), maleic anhydride (MA), and *N*-vinylpyrrolidone (NVP), was synthesized by use of a reversible addition−fragmentation chain transfer (RAFT) process. The terpolymerization was performed in tetrahydrofuran (THF) at room temperature under γ-ray irradiation in the presence of dibenzyl trithiocarbonate (DBTTC). The constants of complex-radical terpolymerization, complex formation, and some kinetic parameters for the monomer systems were studied by UV, ^{1}H NMR, Kelen−Tüdöş methods, respectively. The equilibrium constant (K_2) of 1:1 complex between MA and NVP was determined by UV method as 3.57×10^{-2} L/mol at 293.2 K in $CHCl_3$. Obtained results show that the terpolymerization proceeded mainly through “complex” mechanisms in the state of near-binary copolymerization of St···MA (CTC1) and MA···NVP (CTC2) complexes. And as the big difference in the value of the reactivity ratios between the two complexes ($r_1 = 0.17 \pm 0.01$ and $r_2 = 4.20 \pm 0.34$), the terpolymer displayed the characteristics of “gradient” distribution with controlled molecular weight and narrow molecular weight distribution.

Introduction

Gradient copolymers are copolymers in which the instantaneous composition varies continuously along the chain contour.[1] Controlled free-radical polymerizations are efficient techniques for the synthesis of well-defined gradient copolymers.[2−15] A number of authors have reported the use of atom transfer radical polymerization (ATRP) for the synthesis of statistical copolymers, and several of these reports have targeted the study of the gradient nature of these copolymers.[7−16] Two methods of gradient copolymer synthesis have been reported. The first is the use of batch copolymerization in which a spontaneous gradient in instantaneous composition is formed based on the differences in the reactivity ratios of the comonomers and the concentrations of comonomers in the monomer feed.[7−12,14−15] The second method is the use of semibatch copolymerization to form controlled gradients in instantaneous composition.[7,9,13] The RAFT process is an effective method to synthesize the statistical copolymers,[17−21] but few works have been reported about the synthesis of gradient copolymer.

Batch copolymerization using ATRP to prepare gradient copolymers has been shown to be successful for a number of monomer pairs. The work performed using batch copolymerization has, thus far, focused on styrene-acrylates[7−8,22] and methyl methacrylate−acrylates-based[9,11] gradient copolymers.

In this article, the “gradient” copolymer based on St−MA−NVP was first synthesized by a RAFT process under γ-ray irradiation and by use of the charge-transfer complex effect (CTC) between MA and the other two monomers. The MA−St system was first studied by Mayo and co-workers[23,24] and subsequently by Bamford and Barb,[25,26] Tsuchida et al.,[27,28] and Makuda and Abe.[29] It is well-known that St (donor) and MA (acceptor) form a 1:1 charge-transfer complex (CTC), and this has been confirmed by various methods.[30] On the other hand, this monomer pair is an old but well studied in detail system for demonstration of the complex-radical mechanism of alternating copolymerization.[31,32] The CTC effects were most clearly illustrated in radical terpolymerization of MA with various donor−donor or donor−acceptor vinyl monomers.[30,33−35]

The first poly(MA-*alt*-NVP) was prepared by Morner and Londley (1951).[36] Then the copolymerization of this acceptor−donor monomer system was studied in detail by other researchers.[37−40] Georgiev et al.[41] investigated the influence of the CTC, formed in MA/NVP mixture (CTC is obtained spontaneously when mixing MA and NVP, and the solution is green), on the dominating tendency toward alternating copolymerization of this monomer pair. The copolymerization was carried out in benzene (or toluene) with AIBN initiator under nitrogen atmosphere in adiabatic (with negligible heat loss) and isothermal (349.0 K) conditions. The most active component of the monomer mixture is CTC, which has a very high rate of polar interaction with the growing macroradical. According to the authors, the rapid coordination of CTC with the macroradical in combination with its relatively slow covalent incorporation into the growing chain allows regulation of the effective rate of copolymerization by maintaining a sufficiently low MA concentration in the system. Thus, this is the way to synthesize copolymers with a kinetically regulated structure of the macromolecule.[41]

Alternating copolymers of NVP with MA were synthesized by solution homogeneous or heterogeneous radical copolymerization using various solvents such as benzene or toluene,[41−43] THF,[44] and 1,4-dioxane.[45] Veron et al.[45] have studied the kinetics of radical copolymerization of MA with NVP in dioxane by ^{1}H NMR spectroscopy. It was shown that both monomers had the identical polymerization rates if both monomers were present in the reaction mixture. This is confirmed that MA and NVP copolymerized as a 1:1 complex.

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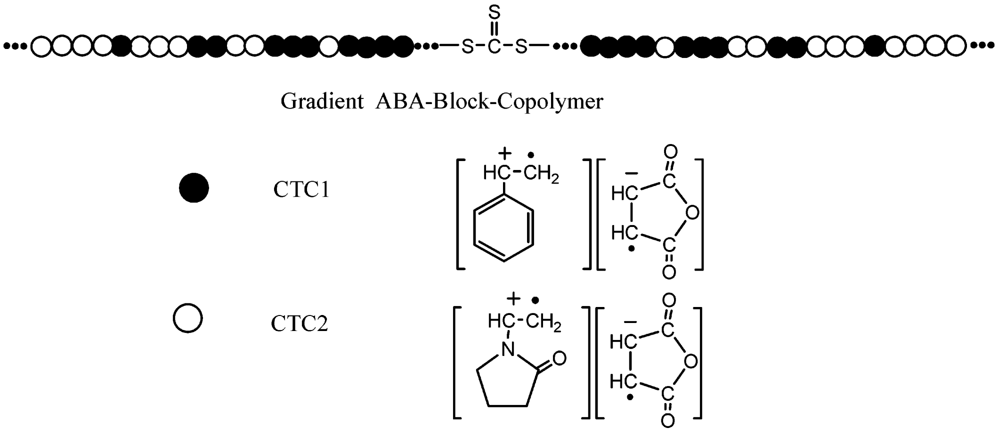
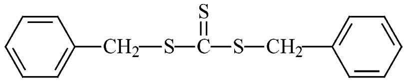
10.1021/ma051997z CCC: $33.50

Scheme 1. Structure of “Gradient” ABA Block Copolymer Composed of Two CTCs



Scheme 2. Structure of Dibenzyl Trithiolcarbonate (DBTTC)



In this work, we select St−MA−NVP terpolymerization system, in which the terpolymerization proceeded mainly through “complex” mechanisms in the state of near-binary copolymerization of St···MA (CTC1) and MA···NVP (CTC2) complexes, the “gradient” ABA-*block*-copolymer formed (more CTC2 in the middle of the polymer, more CTC1 at both ends of the polymer and the trithiocarbonate moiety in the center of the chain) based on the big differences in the reactivity ratio ($r_1 \ll r_2$) and the use of DBTTC described as follows (Scheme 1).

Experimental Section

Materials. MA (99.5%, China National Pharmaceutical Group Corporation) was recrystallized from chloroform prior to use. NVP (98%, Merck) was distilled under reduced pressure in the presence of hydroquinone as inhibitor. St (99%, Shanghai Linfeng Reagent Co.) was distilled from its commercial material before use. DBTTC (Scheme 2), was synthesized as previously described.[46] ^{1}H NMR (500 MHz, CDCl$_3$: δ 4.67 (s, 4H, 2 − CH2−), 7.15−7.25 (m, 10 H, 2 aromatic H) IR: ν 1062.6 cm^{-1} (C=S). Tetrahydrofuran (THF) was freshly distilled over sodium benzophenone ketyl under an argon atmosphere. All other reagents were of analytical grade and used as received.

Copolymerization. Copolymerization reactions of the St−MA−NVP ternary system were carried out in degassed glass tubes in THF solution initiated by γ-ray (^{60}Co radiation source) at dose rate 50Gy/min in the presence (or absence) of DBTTC. After polymerization for a given time, the reaction mixture was poured into a large amount of chloroform to precipitate the copolymer, and the powderlike product obtained was separated by filtration; it was then purified by multiple washing in hot benzene and in diethyl ether and was redeposited by centrifugation. The copolymer compositions were determined by elementary analysis (EA) and FTIR spectroscopy.

Measurements. FTIR spectra were recorded on a VECTOR22 FTIR spectrometer using a KBr pellet. ^{1}H NMR spectra (400 MHz) were taken on a Bruker ACF spectrometer using deuterium acetone as the solvent. UV spectra were recorded on a Shimadzu UV-2401PC spectrometer using CHCl$_3$ as the solvent. EA were performed at a Elementar Vario EL-IIIapparatus.

Copolymerization constants (r_1K_1/K_2 and r_2K_2/K_1; K_1 and K_2 are equilibrium constants for monomer CTCs; r_1 and r_2 represent the reactivity ratios between the two CTCs) of complexed monomer pairs were determined by the Kelen−Tüdöş[47] and Fineman−Ross[48] methods.

Copolomerization kinetics was studied by the gravimetric method.

The average molar mass and molar mass distribution of the copolymers were measured on a Waters 515 gel permeation chromatography (GPC) equipped with 10^3, 10^4, and 10^5 Å waters UltraStyragel columns, and using THF as eluent at a flow rate of 1.0 mL/min. Monodisperse polystyrene was used as calibration standards.

Results and Discussion

1. Charge-Transfer Complex Formation. From the donor−acceptor properties of the studied monomers the formation of the following equimolar (1:1) CTC between MA and St may be predicted:

$$\mathrm{MA} + \mathrm{St} \overset{K_1}{\rightleftharpoons} [\mathrm{MA}\cdots\mathrm{St}] \tag{1}$$

(K_1 = 0.34 L/mol in *n*-hexane at 303.2 K and 0.24 L/mol in CHCl$_3$ at 298.2 K)[28,49]

The equilibrium constant (K_2) of 1:1 complex between MA and NVP are determined by UV method with the use of the Bensei−Hildbrand[50] method and the Scott equation[51] (eq 2).

$$\frac{l}{d}[\mathrm{A}]_0[\mathrm{D}] = \frac{1}{\epsilon K} + \frac{[\mathrm{D}]}{\epsilon} \tag{2}$$

Here $[\mathrm{A}]_0$ is the initial concentration of acceptor, [D] is the concentration of donor, l is the optical path length, d is the absorbance at given wavelength, ϵ is the extinction coefficient of the CTC, and K is the equilibrium constant of the complex.

The concentration of acceptor monomer (MA) in different mixtures with NVP at [NVP] ≫ [MA] was constant at 0.2 mol/L in CHCl$_3$. The concentration of NVP varied from 0.8 to 3.0 mol/L. The absorbance d at 375 nm was recorded by UV spectroscopy. Then, from the plot of [NVP][MA]l/d vs [NVP] complex formation constant (K_2) is calculated (Figure 1). The value of K_2 for the MA···NVP complex is 3.57×10^{-2}L/mol at 293.2 K in CHCl$_3$.

2. Complex-Radical Terpolymerization. 2.1. Mechanism. The ternary monomer system studied can be classified as donor (St)−acceptor (MA)−donor (NVP) system, which can be characterized as follows: (1) The acceptor−donor pairs of MA−St and MA−NVP have a tendency to give complex formation. (2) MA is a powerful electron acceptor. In common with many of strong donor and acceptor molecules it is difficult to homopolymerize but enters into a copolymerization reaction with considerable ease when the comonomers are donors. (3) As the $G(R)$ value (the yield of free radicals per 100 eV absorption of radiation energy) of St is small (only 0.69),[52,53] and styrene has

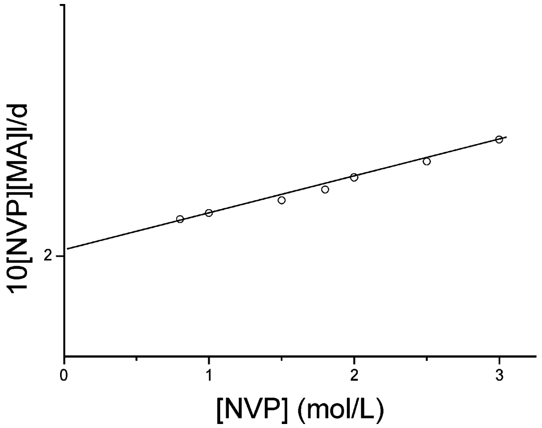


Figure 1. Scott plot (10[NVP][MA]l/d vs [NVP]) of the MA-NVP complex in CHCl3 at 375 nm and 293.2 K obtained by UV method: $1/\epsilon K$ is the intercept on the *Y*-axis, tan $\alpha = 1/\epsilon$, where *l* is the optical path length, *d* is the absorbance, and ϵ is the extinction coefficient of the CTC.

a low propagation coefficient at ambient temperature ($k_p = 86$ L mol^{-1} s^{-1}),[54] the conversion of styrene homopolymerization will not be high. Previous work[55] has confirmed this result. In this work, the similar result was obtained from the kinetics analysis studied by gravimetric (Figure 2) and ^{1}H NMR (Figure 3) methods for the copolymerization between St and NVP. Little or no copolymer content of St and NVP was found in synthesis with an increase of reaction time even to 6 h. (At this time, the terpolymerization has been completed.) From the NMR spectra, a few of homopolymers of NVP could be found after 6 h. (The integrated areas of the peaks of the protons numbered as 5, 6, and 7 decreased a little with the increase of the irradiation time.) But for the much larger reactivity of the complex copolymerization between the donor−acceptor monomers, the homopolymerization of NVP can be ignored in the St−MA−NVP terpolymerization system. So the terpolymerization proceeded mainly through “complex” mechanisms in the state of near-binary copolymerization of St···MA and MA···NVP complexes.

On the base of these selective characteristics of self-organized ternary systems studied, elementary stages of propagation reactions in the condition of stationary kinetics (≤10% conversion) can be proposed as follows:

Initiation:

$$\mathrm{MA} + \mathrm{St} \overset{K_1}{\rightleftharpoons} \mathrm{CTC1} \xrightarrow{\gamma\text{-ray}} \mathrm{CTC1}^{\bullet} \tag{3}$$

$$\mathrm{MA} + \mathrm{NVP} \overset{K_2}{\rightleftharpoons} \mathrm{CTC2} \xrightarrow{\gamma\text{-ray}} \mathrm{CTC2}^{\bullet} \tag{4}$$

Propagation:

$$\mathrm{CTC1}^{\bullet} + \mathrm{CTC1} \rightarrow (\mathrm{CTC1})_n^{\bullet} \tag{5}$$

$$\mathrm{CTC1}^{\bullet} + \mathrm{CTC2} \rightarrow -(\mathrm{CTC2})_n-(\mathrm{CTC1})^{\bullet} \tag{6}$$

$$\mathrm{CTC2}^{\bullet} + \mathrm{CTC1} \rightarrow -(\mathrm{CTC1})_n-(\mathrm{CTC2})^{\bullet} \tag{7}$$

$$\mathrm{CTC2}^{\bullet} + \mathrm{CTC2} \rightarrow (\mathrm{CTC2})_n^{\bullet} \tag{8}$$

2.2. Determination of the Reactivity Ratios (r_1 and r_2). To determine the relative activity of St···MA and MA···NVP complexes, the copolymerizations were carried out under the following conditions: constant concentration of MA (50 mol %) to ensure the complex formation to a maximum extent and low conversion (≤10%), as shown in Table 1.

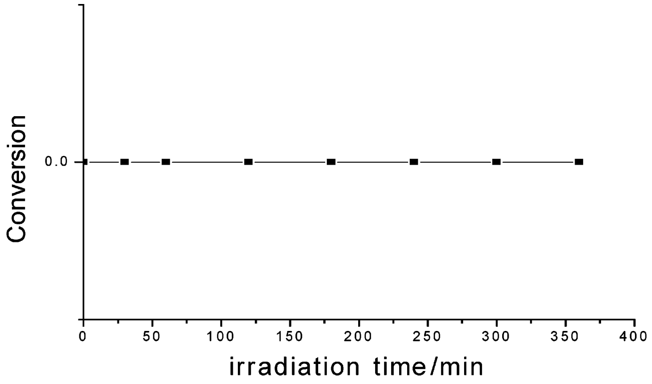


Figure 2. Kinetics curve of copolymerization of St and NVP in THF under irradiation at dose rate 50Gy/min.

The reactivity ratios of two CTCs are calculated with the modified terminal model of Kelen−Tüdöş and Fineman−Ross equation in the following form:

$$\eta = [r_1(K_1/K_2) + r_2(K_2/K_1)/\alpha]\xi - r_2(K_2/K_1)/\alpha \tag{9}$$

Here $\xi = (F^2/f)/(F^2/(f + \alpha))$, $\eta = [F(f - 1)/f]/(F^2/(f + \alpha))$, $\alpha = \sqrt{(F^2/f)_{\min}(F^2/f)_{\max}}$, K_1 and K_2 are the constants of complex formation for St···MA and MA···NVP complexes, respectively, $F = M_1/M_2$ = [St···MA]/[MA···NVP], $f = m_1/m_2$.

Using the Kelen−Tüdöş (KT) and Fineman−Ross (FR) equations on the basis of experimental data shown in Table 1, from plots of η vs ξ (Figure 4) and $F(f - 1)/f$ vs F^2/f (Figure 5), respectively, copolymerization constants were calculated: $r_1K_1/K_2 = 1.14 \pm 0.04$ and $r_2K_2/K_1 = 0.62 \pm 0.05$ by the KT method; $r_1 = 0.17 \pm 0.01$ and $r_2 = 4.20 \pm 0.34$ (taking into account K_1 and K_2 constants); by the FR method, $r_1K_1/K_2 = 1.19 \pm 0.05$ and $r_2K_2/K_1 = 0.72 \pm 0.16$; $r_1 = 0.18 \pm 0.01$ and $r_2 = 4.84 \pm 1.07$. It is notable that although r_2 is much larger than r_1, however, from Table 1 we can find that $m_1 > M_1$ and $m_2 < M_2$ which shows the “observable reactivity” of St···MA is larger than that of MA···NVP. It means that the “observable reactivities” of the complexes are determined by the “reactivity coefficient ratio” ($r_1(K_1/K_2)$ for St···MA and $r_2(K_2/K_1)$ for MA···NVP complex) rather than by the reactivity ratio in the present case. The so-called “reactivity coefficient ratio” depend on not only the reactivity ratios, but also the equilibrium constants of the charge-transfer complexes.

3. Synthesis of “Gradient” Copolymers. Reversible addition−fragmentation chain transfer (RAFT) polymerization has been the focus of intensive research over the past few years since this methodology allows the synthetic tailoring of macromolecules with complex architectures including block,[56−57,60−61] graft,[59] comb,[60] and star[58] structures with predetermined molecular weight, terminal functionality, and narrow molecular weight distribution. Initiation is accomplished utilizing conventional thermal, photochemical, redox, or γ-irradiation methods. Poly(styrene-*alt*-maleic anhydride) was successfully obtained by use of RAFT method under γ-ray irradiation.[62] But for gradient copolymer based on complex-radical terpolymerization, RAFT polymerizations have not been previously reported.

3.1. RAFT Polymerization of “Gradient” Copolymer. DBTTC was chosen as RAFT chain transfer agent (CTA). Other work[62−64] shows that in the presence of DBTTC, some (co)-polymers with well-defined structures, controlled molecular weight, narrow molecular weight distribution (M_w/M_n) could be obtained under γ-ray radiation.

Typical GPC curves of copolymerization of St, MA, and NVP throughout the polymerization are shown in Figure 6. The MWDs of the polymers obtained remain narrow throughout the copolymerization, and the PDIs are in the range from 1.47 to

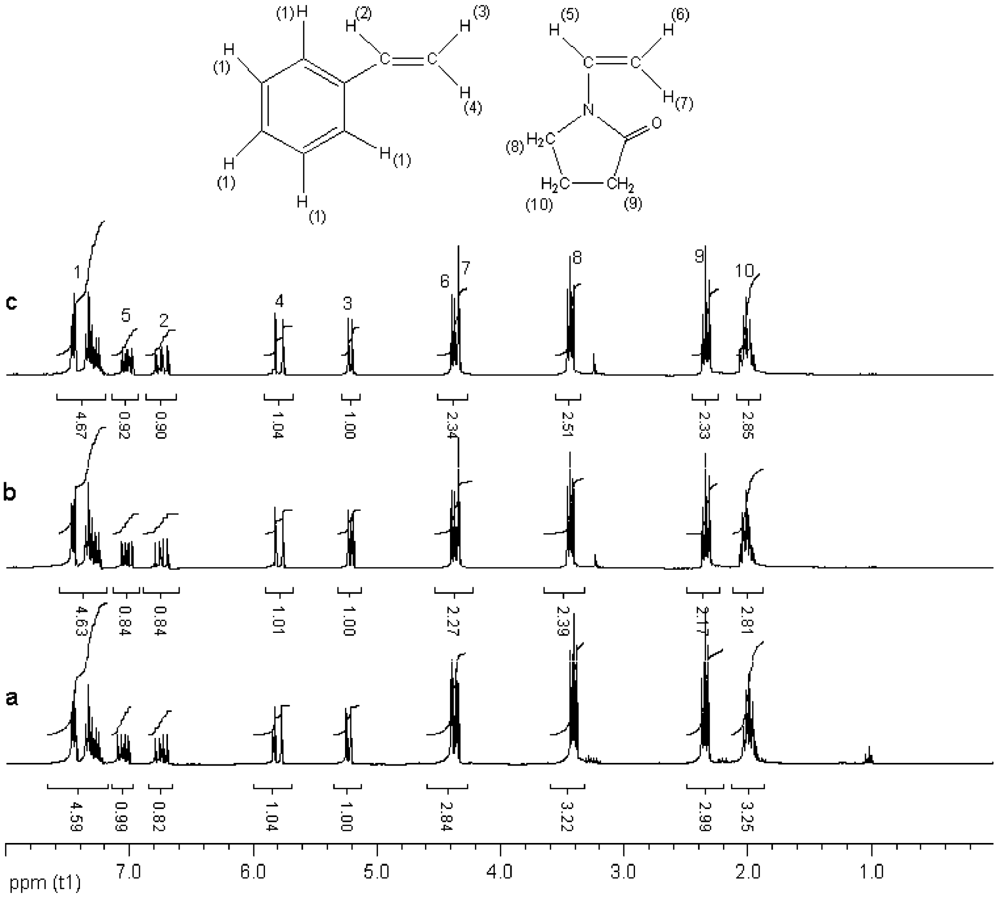


Figure 3. ^{1}H NMR analysis of copolymerization of St and NVP in CH_3COCH_3-d_6 under irradiation at dose rate 50Gy/min: (a) before irradiation; (b) after 1 h under γ-rays; (c) after 6 h under γ-rays.

Table 1. Copolymerization of St···MA (CTC1) Complex with MA···NVP (CTC2) Complex in THF

monomer feed (mol %)		conversion	acid no.	N content	copolymer composition (mol %)		by KT method		by FR method	
M_1	M_2	(%)	(mg of KOH/g)	(%)	m_1	m_2	η	ξ	F^2/f	$F(f-1)/f$
20	80	2.35	543	4.97	26.44	73.56	−0.343	0.134	0.174	−0.446
40	60	2.88	542	3.52	48.30	51.70	−0.029	0.297	0.476	−0.047
50	50	2.68	544	2.91	57.39	42.61	0.138	0.398	0.742	0.258
60	40	2.74	543	2.36	65.54	34.46	0.308	0.513	1.183	0.711
80	20	2.85	543	1.27	81.56	18.44	0.653	0.763	3.617	3.095
90	10	3.01	542	0.57	91.77	8.23	0.978	0.866	7.264	8.1933

1.17 upon various conversions. The linear increase of the molar masses as a function of the monomer conversion and the PDIs around 1.2 are indicative of a controlled growth of the polymer chains (Figure 7).

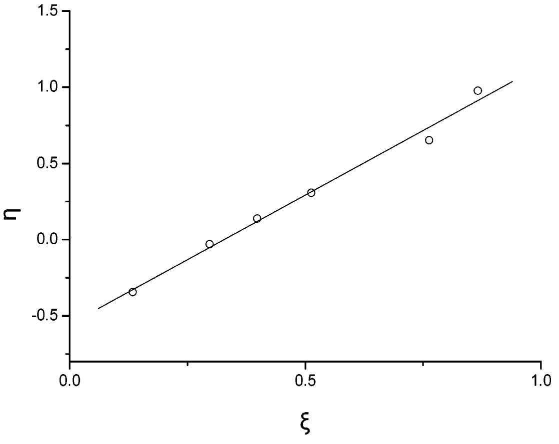
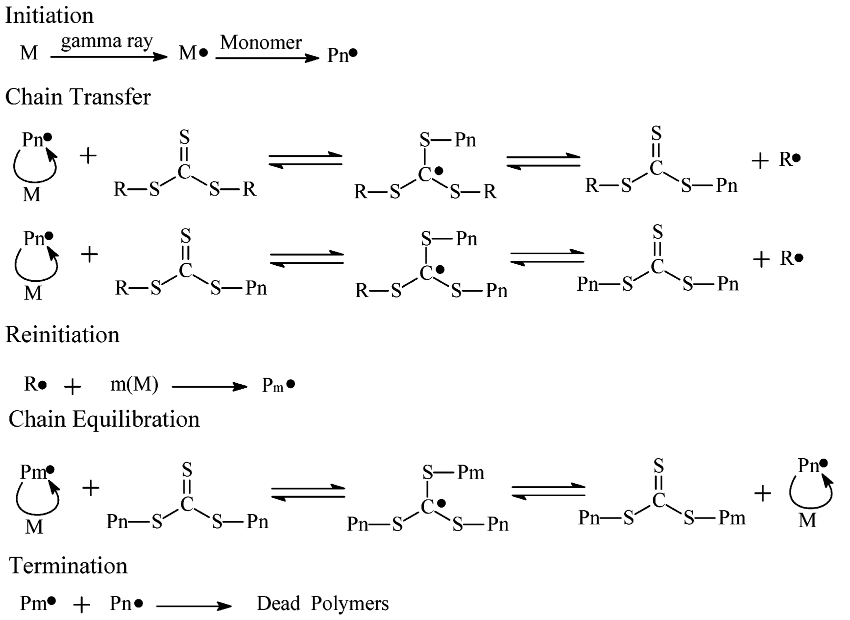


Figure 4. Kelen−Tudos plots for the copolymerization of St···MA (CTC1) with MA···NVP (CTC2) in THF initiated by γ-ray radiation. tan α = $r_1(K_1/K_2) + r_2(K_2/K_1)/\alpha$ and intercept $-r_2(K_2/K_1)/\alpha$.

To determine the “gradient” nature of copolymer, the N content and acid number were obtained by elementary analysis and potentiometric titration, respectively. Linear decrease of the N content of the copolymer with increase of conversion shown in Figure 8 indicates that the NVP···MA complex varies continuously along the chain contour. The acid number is nearly changeless to about 543 mgKOH/g (meaning Ma mol % in the copolymer to about 50) with the increase of conversion (Figure 9) as described previously.

3.2. Mechanism. The mechanism by which the process imparts living character to the polymerization is shown in Scheme 3 and is carried out by simply introducing a suitable thiocarbonylthio compound to an otherwise conventional radical polymerization. During the first stage of the polymerization the RAFT agent is consumed by propagating radicals by an addition−fragmentation mechanism. The fragmented radical ($R^\bullet$) reinitiates polymerization, resulting in new propagating radicals which then take part in the equilibrium established between the

Scheme 3. RAFT^a Process[65]



^{a} M is monomer; R is benzyl group; P*n* and P*m* are polymer chains.

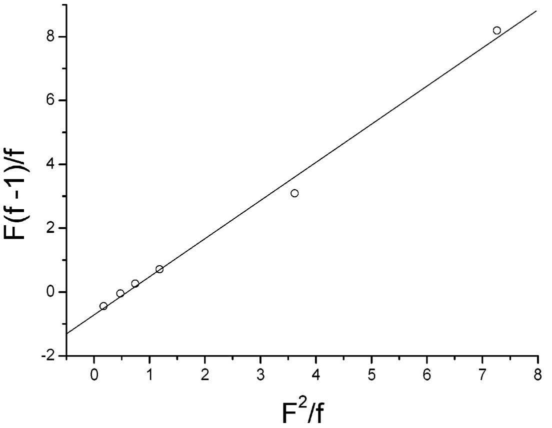


Figure 5. Fineman−Ross plots for the copolymerization of St···MA (CTC1) with MA···NVP. (CTC2) in THF via γ-ray radiation. tan $\alpha = r_1(K_1/K_2)$ and intercept $-r_2(K_2/K_1)$.

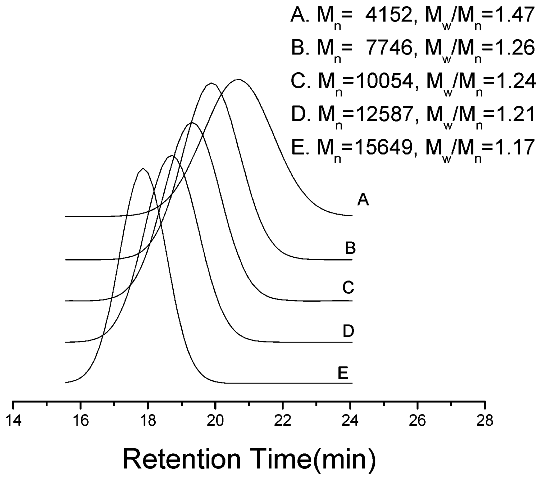


Figure 6. GPC traces of terpolymerization of St (0.0125 mol), MA (0.0250 mol), and NVP (0.0125 mol) in 2 mL of THF in the presence of DBTTC (0.10 mmol).

dormant polymer and active chains. The equilibration process allows all chains produced to grow in a uniform manner, resulting in narrow polydispersity polymers.

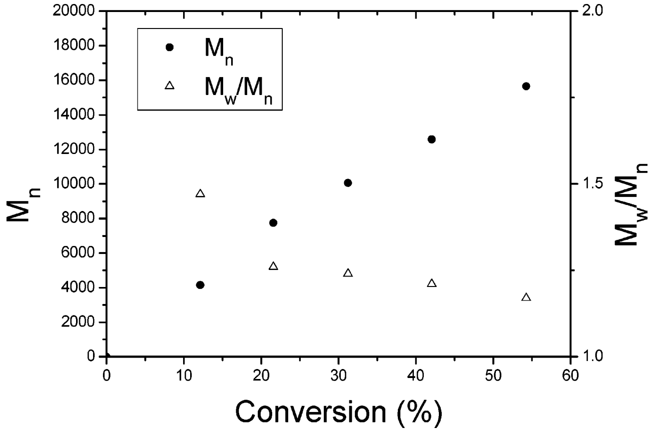


Figure 7. Variation of M_n and M_w/M_n (PDI) with conversion for the terpolymerization of St (0.0125 mol), MA (0.0250 mol), and NVP (0.0125 mol) in 2 mL of THF in the presence of DBTTC (0.10 mmol).

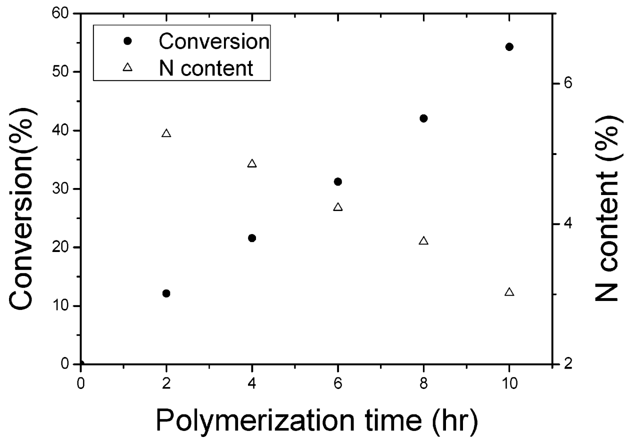
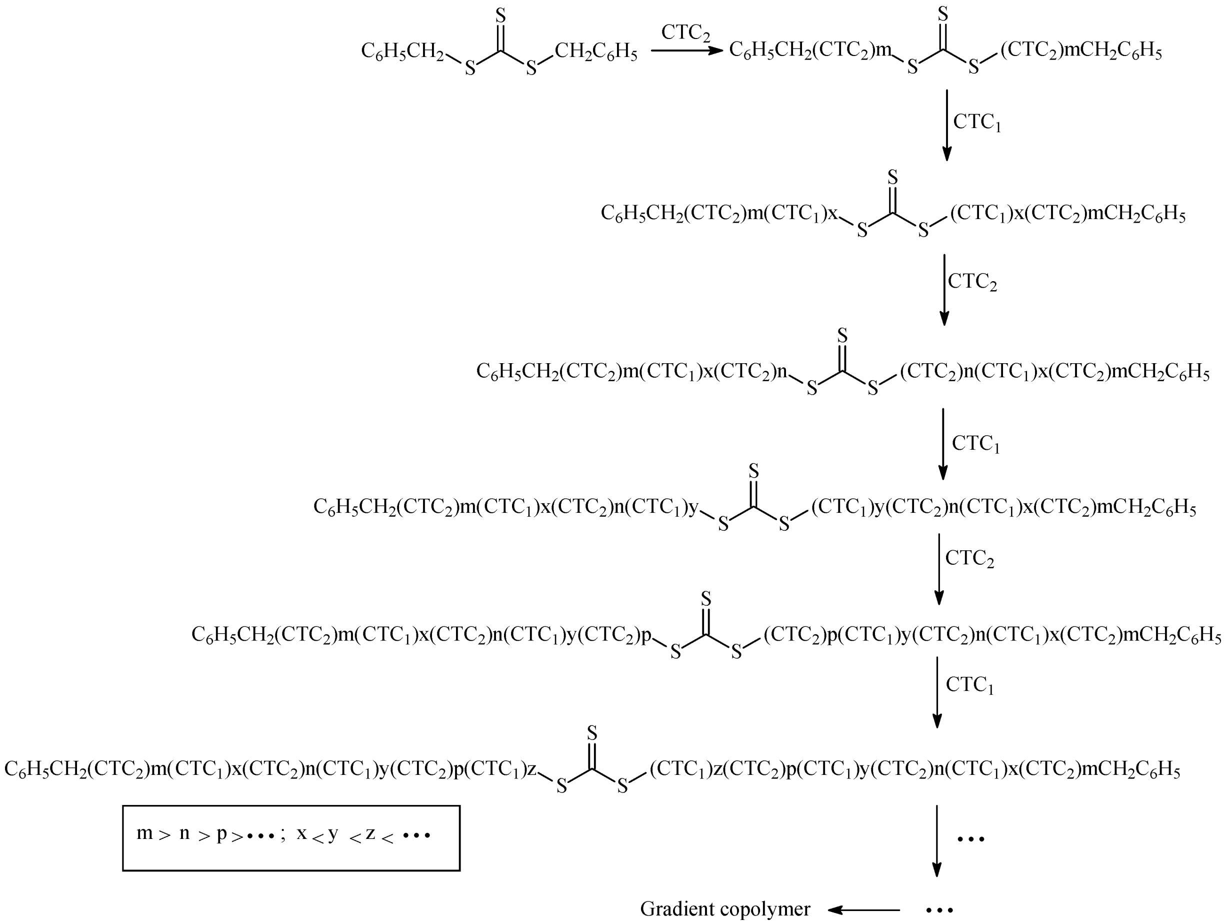


Figure 8. Dependence of N content of copolymer on polymerization time for the terpolymerization of St (0.0125 mol), MA (0.0250 mol), and NVP (0.0125 mol) in 2 mL of THF in the presence of DBTTC (0.10 mmol).

In this work, dibenzyl trithiocarbonate was used as CTA which was shown to have useful structural characteristics as it can accommodate two leaving groups attached to the sulfur

Scheme 4. Proposal Used to Create Gradient Copolymer[a]



[a] CTC_1 and CTC_2 are [St•••MA] and [MA•••NVP] complexes, respectively.

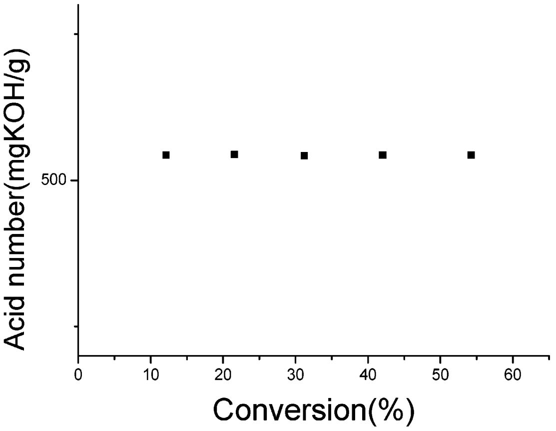


Figure 9. Dependence of acid number of copolymer on conversion for the terpolymerization of St (0.0125 mol), MA (0.0250 mol), and NVP (0.0125 mol) in 2 mL of THF in the presence of DBTTC (0.10 mmol).

atoms. Other work[66] shows that both benzyl groups act as leaving groups such that the trithiocarbonate moiety is in the center of the chain. This compound should have a higher transfer coefficient than a monobenzyl compound because there are two pathways for fragmentation from the intermediate adduct.

A proposal used to create gradient copolymer is shown in Scheme 4. Using the big difference in the value of r_1 and r_2 of the two CTCs, the copolymerization proceeded in one step. While the reaction time increases, the concentration of the CTCs behaves regular changes (the concentration of CTC2 decreases much faster than its of CTC1.). The “gradient” ABA block copolymers are obtained.

Conclusions

A one-step process using RAFT process to synthesize a novel “gradient” copolymer based on complex-radical terpolymerization of St, MA and NVP initiated by γ-rays was demonstrated. A well-defined macromolecular structure and composition could be obtained via this method.

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