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Complex-radical terpolymerization of styrene, maleic anhydride, and *N*-vinyl pyrrolidone via γ-ray radiation: Synthesis, characterization, and micellization

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Abstract

Radical terpolymerization of donor–acceptor monomers, i.e. styrene (St), maleic anhydride (MA) and *N*-vinyl pyrrolidone (NVP) were carried out in methyl ethyl ketone(MEK) under γ-ray radiation at room temperature. Constants of copolymerization, complex formation, and some kinetic parameters for the monomer systems were studied by UV, ^{1}H NMR, Kelen-Tüdöş and Fineman-Ross methods, respectively. Obtained results show that terpolymerization proceeded mainly through 'complex' mechanisms in the state of near-binary copolymerization of St···MA and MA···NVP complexes. The homo-polymerization of St and NVP and the copolymerization between St and NVP could hardly be occurred. The possible reason is the effect of protection from radiation by styrene with its aryl-ring structure and/or the much larger reactivity of the complex copolymerization between the donor–acceptor monomers. The terpolymer self-assembles into micelles in aqueous solution. Polymeric micelles, composed of chains of St–MA and MA–NVP with equal molar ratio, displayed narrow size distribution of about 120 nm. The critical association concentration of micelles was determined to be around 3 mg/L.

Keywords: Charge transfer complex; Gamma ray radiation; Micellization

1. Introduction

It is well known that complex-radical copolymerization of donor–acceptor binary and ternary monomer systems is an effective method for the synthesis of functional macromolecules with given composition, structure and properties [1–7].

In some earlier publications, a number of systematic studies were carried out for the terpolymerization of MA, styrene, and donor- or acceptor-type monomers such as unsaturated epoxides [8], acrylics [9–13], vinyltriethoxysilane [14], citraconic anhydride [7], and certain maleimides [15]. All of these terpolymers were obtained in the presence of the initiator. Some showed high thermal stabilities [8–10].

In this study, the terpolymerization of MA, styrene, and NVP were carried out in MEK at room temperature, and γ-ray irradiation from ^{60}Co source as a convenient and effective initiation method [16,17] was used to initiate the complex-radical copolymerization; such work has scarcely been reported before. St and NVP were found to form charge transfer complex (CTC) with MA [18–22]. The complex-radical copolymerization of St–MA and St–NVP can be predicted. For the effect of protection from radiation by styrene and/or the much larger reactivity of the complex copolymerization between the donor–acceptor monomers, the homopolymerization of St and NVP and the copolymerization between St and NVP could hardly be occurred. The kinetics and mechanism of terpolymerization and the determination of terpolymer composition were investigated by UV, ^{1}H NMR, FTIR, elementary analysis (EA), Kelen-Tüdöş, Fineman-Ross and gravimetric methods, respectively. Moreover, the self-assembly of the terpolymer has been extensively studied in aqueous solution.

2. Experimental

2.1. 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 hydroquinoe as inhibitor. St (99%, Shanghai

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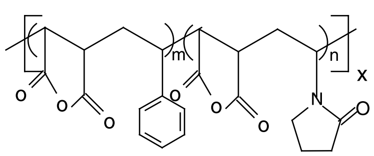
Linfeng Reagent Company) was distilled from its commercial material before use. Other reagents were purified by ordinary methods.

2.2. Copolymerization

Copolymerization reactions of the St–MA–NVP ternary system were carried out in degassed glass tubes in MEK initiated by γ-ray (^{60}Co radiation resource) at dose rate 50 Gy/min. After polymerization for a given time ($\leq 10\%$ conversion), 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 and FTIR spectroscopy.

The terpolymer synthesized by use of molar ratio of initial monomers St:MA:NVP = 1:2:1 had following characteristics:



m = 0.48 and n = 0.52

Acid number (AN) 542.4 mg KOH/g, N content 2.97% (by elemental analysis). FTIR spectra, cm^{-1}: $\nu_{C=O}$ 1780 (anhydride unit), 1720 and 1635 (pyrrolidone unit), $\nu_{C\text{–}O\text{–}C}$ 1180 (anhydride unit), δ_{CH} 1080 and 700 (mono-substituted benzene ring).

2.3. 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 a solvent. UV spectra were recorded on a Shimadzu UV-2401PC spectrometer using $CHCl_3$ as a solvent. EA were performed at a Elementar Vario EL-apparatus.

Copolymerization constants (r_1K_1/K_2 and r_2K_2/K_1, K_1 and K_2 are equilibirum constants for monomer CTCs) of complexed monomer pairs were determined by the modified Kelen-Tüdöş [23] and Fineman-Ross methods [24].

Copolomerization kinetics were studied by gravimetric method.

The particle size of polymeric micelles were determined by dynamic light scattering (DLS) in water at 298.2 K. A modified commercial laser light scattering (LLS) spectrometer (ALV/SP-125) equipped with a multi-tdigital time correlator (ALV-5000) and a solid-state laser (ADLAS DPY 425II, output power ~400 mW at $\lambda_0 = 532$ nm) was used. The details of the LLS theory and instrumentation can be found elsewhere [25,26]. In DLS, the measured intensity–intensity time correlation function was analyzed by both the Laplace inversion (CONTIN) and cumulant programs in the correlator, which led to the hydrodynamic radius distribution ($f(R_h)$) and the average hydrodynamic radius (R_h) of the micelles.

The critical association concentration (CAC) of micelles was determined by the modified largest gas bubbles method [27] in water at 298.2 K.

3. Results and discussion

3.1. Charge transfer complex formation

From the donor–acceptor properties of the studied monomers it may be predicted that the formation of the following equimolar (1:1) CTC between MA and St:

$$MA + St \overset{K_1}{\rightleftarrows} [MA \cdots St] \times (K_1 = 0.34\ \text{L/mole in}\ n-\text{hexane at 303.2 K and 0.24 L/mole in}\ CHCl_3\ \text{at 298.2 K})\ [28,29] \quad (1)$$

The equilibrium constant (K_2) of 1:1 complex between MA and NVP are determined by UV method with use of the Bensei-Hildbrand [30] method and Scott equation [31]. 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 spectrum. Then, from the plot of [NVP][MA]l/d vs. [NVP] the complex formation constant (K_2) is calculated (Fig. 1). The value of K_2 for MA···NVP complex is 3.57×10^{-2} L/mol at 293.2 K in $CHCl_3$.

The difference in the values of K_1 and K_2, which is conditioned by the structural characteristics of donor monomers, causes the formation of terpolymers with different ratios of St and NVP units at different reaction periods (Table 1).

3.2. Complex-radical terpolymerization

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, MA–NVP have tendency to the complex-formation; (2) MA does not homopolymerize in selected conditions of terpolymerization; (3) As the $G(R)$ value (the yield of free

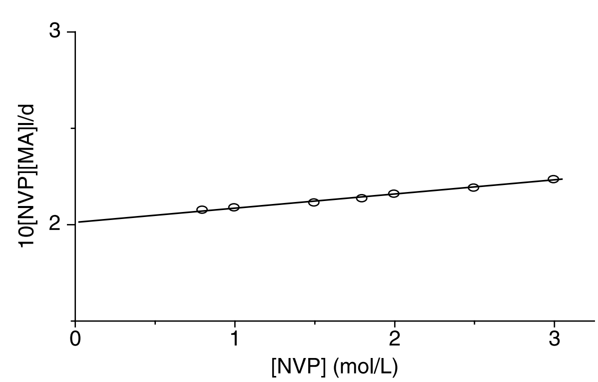


Fig. 1. Scott plot (10[NVP][MA]l/d vs.[NVP] of the MA–NVP complex in $CHCl_3$ at 375 nm and 293.2 K obtained by UV method: l/e K is the intercept on the Y-axis, tan $a = l/e$, where l is the optical path length and e is the extension coefficient of the CTC.

Table 1
Copolymerization of St···MA (M_1) complex with MA···NVP (M_2) complex in MEK

Monomer feed (mol%)		Conversion (%)	Acid number (mgKOH/g)	N content (%)	Copolymer composition (mol%)		By KT method		By FR method	
M_1	M_2				m_1	m_2	η	ξ	F^2/f	$F(f-1)/f$
20	80	2.35	543	4.91	27.34	72.63	−0.390	0.156	0.166	−0.414
30	70	2.68	544	4.32	36.29	63.71	−0.266	0.264	0.322	−0.324
50	50	2.74	543	2.40	64.95	35.05	0.320	0.376	0.540	0.460
70	30	2.85	543	1.37	80.10	19.90	0.780	0.601	1.353	1.753
90	10	3.01	542	0.39	94.36	5.64	1.475	0.844	4.841	8.462

radicals per 100 eV of absorbed radiation) of St is only 0.05 (the effect of protection from radiation by styrene), [32] the copolymerization between St and NVP could hardly be occurred. At the same time, the homopolymerzation of St and NVP are restrained by the formation of MA–St, MA–NVP complexes. This can be confirmed by kinetics analysis studied by gravimetric (Fig. 2) and ^{1}H NMR (Fig. 3) methods. For the binary system of St and NVP, almost no polymer was found to be synthesized with the increase of reaction time even to 6 h. So the terpolymerization proceeded mainly through 'complex' mechanisms in the state of near-binary copolymerization of St···MA and MA···NVP complexes.

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

Initiation:

$$\underset{\text{CTC1}}{[\text{MA}\cdots\text{St}]} \xrightarrow{\gamma\text{-ray}} \underset{\text{CTC1}\cdot}{[\text{MA–St}]\cdot} \quad (2)$$

$$\underset{\text{CTC2}}{[\text{MA}\cdots\text{NVP}]} \xrightarrow{\gamma\text{-ray}} \underset{\text{CTC2}\cdot}{[\text{MA–NVP}]\cdot} \quad (3)$$

Propagation:

$$\text{CTC1}\cdot + \text{CTC1} \rightarrow (\text{CTC1})_m\cdot \quad (4)$$

$$\text{CTC1}\cdot + \text{CTC2} \rightarrow (\text{CTC1})-(\text{CTC2})_n\cdot \quad (5)$$

$$\text{CTC2}\cdot + \text{CTC1} \rightarrow (\text{CTC2})-(\text{CTC1})_n\cdot \quad (6)$$

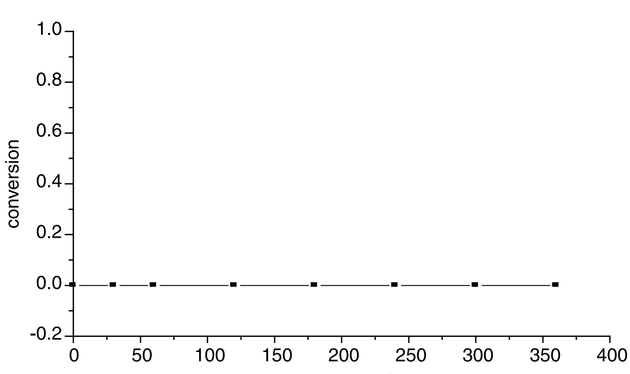


Fig. 2. Kinetics curve of copolymerization of St and NVP in MEK under irradiation at dose rate 50 Gy/min.

$$\text{CTC2}\cdot + \text{CTC2} \rightarrow (\text{CTC2})_n\cdot \quad (7)$$

Termination:

Binary-radical combination.

Firstly, the two CTCs are transformed to complex radicals induced by gamma ray irradiation. Then these radicals combine with the initial CTCs to actualize the chain growth. When any two complex radicals react with each other, the corresponding chain grouth reaction is terminated.

Therefore, to determine the relative activity of St···MA and MA···NVP complexing monomers, terpolymerization was carried out under the conditions that ensure the complex-formation to a maximum extent: with the constant concentration of MA (50 mol%) and condition copolymerization (≤10% conversion), as shown in the Table 1.

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

$$\eta = \left[r_1\left(\frac{K_1}{K_2}\right) + r_2\left(\frac{K_2/K_1}{\alpha}\right)\right]\xi - r_2\left(\frac{K_2/K_1}{\alpha}\right) \quad (8)$$

and

$$\frac{F(f-1)}{f} = r_1\frac{(K_1/K_2)F^2}{f} - r_2\left(\frac{K_2}{K_1}\right) \quad (9)$$

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

Using the Kelen-Tüdöş (KT) and Fineman-Ross (FR) equations on the base of experimental data shown in

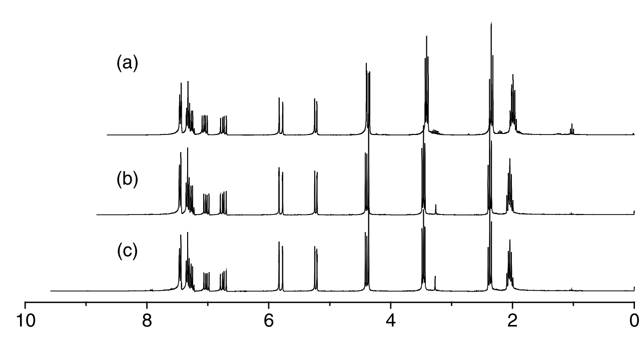


Fig. 3. ^{1}H NMR analysis of copolymerization of St and NVP in CH_3COCH_3-d_6 under irradiation at dose rate 50 Gy/min. (a) Before irradiation; (b) 1 h under gamma ray; (c) 6 h under gamma ray.

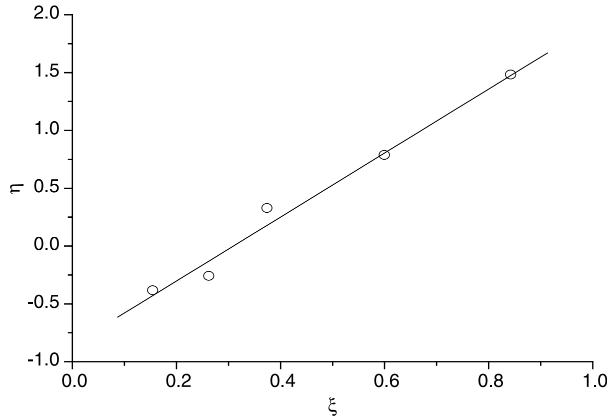


Fig. 4. Kelen-Tüdöş plots for the copolymerization of ST⋯MA (M_1) with MA⋯NVP (M_2) in MEK via gamma ray radiaion. tan $a = r_1(K_1/K_2) + r_2(K_2/K_1)/a$ and intercept $-r_2(K_2/K_1)/a$.

the Table 1 from plots of η vs. ξ (Fig. 4) and $F(f-1)/f$ vs. F^2/f (Fig. 5), respectively, copolymerization constants were calculated: $r_1(K_1/K_2) = 1.91$ and $r_2(K_2/K_1) = 0.77$ by KT method; $r_1 = 0.28$ and $r_2 = 5.18$ (taking into account K_1 and K_2 constants); and by FR method, $r_1(K_1/K_2) = 1.14$ and $r_2(K_2/K_1) = 0.76$; $r_1 = 0.17$ and $r_2 = 5.11$. The results indicate that the MA⋯NVP complex is more active in the radical copolymerization than St⋯MA complex.

3.3. Micellization of the terpolomers

Because of the difference in the value of r_1 and r_2, the terpolymers formed like ‘gradient’ polymer in which the concentration of MA–NVP chains varies in a continuous way from one side to the other. And for the hydrophilic properties of MA–NVP chains, the terpolymers can self-assemble in aqueous solution to form micelles as diblock copolymer do [33]. The size of micelles was measured by DLS at different concentrations. As shown in Fig. 6, the micelles in water at a concentration of 1.5 mg/mL, composed of the chains of St–MA

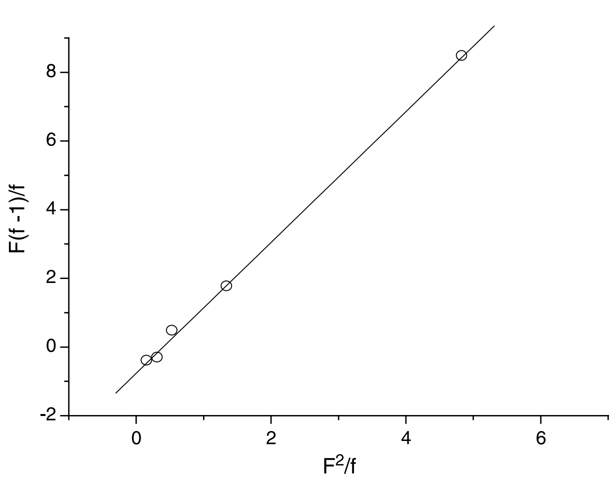


Fig. 5. Fineman-Ross plots for the copolymerization of St⋯MA_n (M_1) with MA_n⋯NVP (M_2) in MEK via gamma ray radiation. tan $a = r_1(K_1/K_2)$ and intercept $-r_2(K_2/K_1)$.

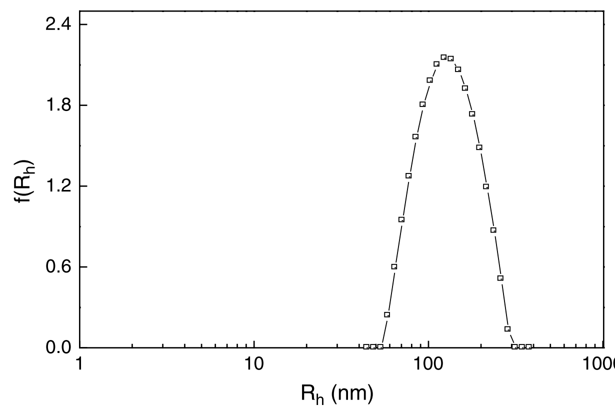


Fig. 6. Size distribution of micelles in water composed of chains of St–MA_n and MA_n–NVP with equal molar ratio measured by DLS.

and MA–NVP with equal molar ratio, featured a narrow size distribution with the average diameter about 120 nm.

The modified largest gas bubbles method was used to determine the critical association concentration (CAC) of micelles. Through surface tension measurements for micelles at different concentrations, the CAC of micelles composed of the chains of St–MA and MA–NVP with equal molar ratio was obtained about 3 mg/L (Fig. 7).

4. Conclusions

Complex-radical terpolymerization of styrene, maleic anhydride and *N*-vinyl pyrrolidone were successfully performed in methyl ethyl ketone (MEK) under γ-ray radiation at room temperature. Obtained results show that the terpolymerization proceeded mainly through ‘complex’ mechanisms in the state of near-binary copolymerization of St⋯MA and MA⋯NVP complexes. And for the difference in the value of r_1 and r_2 ($r_1 \ll r_2$) and the hydrophilic properties of MA–NVP chains, the terpolymers can self-assemble in aqueous solution to form micelles.

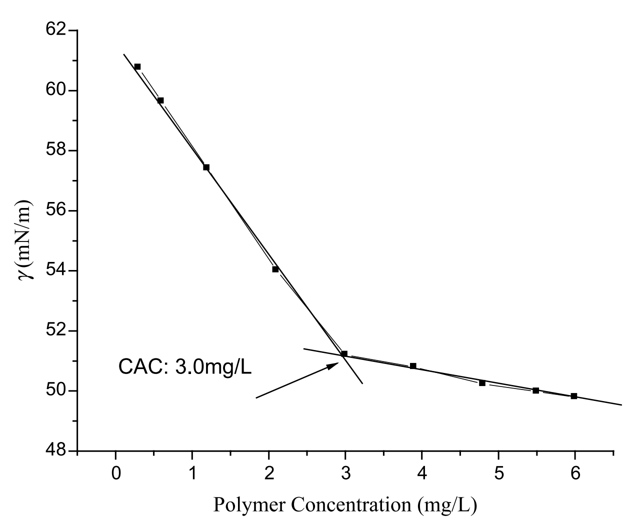


Fig. 7. Dependence of surface tension on polymer concentration of micelles composed of chains of St–MA and MA–NVP with equal molar ratio in water at 298.2 K.

As the poly(NVP) is known to be quite biocompatible and to improve adhesion [34], these polymeric self-assemblies based on the terpolymers are hoped to be used as drug carriers for parenteral administration.

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