

EFFECTS OF SOLVENT POLARITY ON FREE RADICAL COPOLYMERIZATION OF 5-HEXENOIC ACID AND ACRYLONITRILE

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ABSTRACT

The effects of solvent polarity on free radical copolymerization of 5-hexenoic acid and acrylonitrile at 60°C were studied. It was observed that as the polarity of solvents enhanced, both the copolymerization rate and the reactivity ratios r_1 , r_2 increased, while the alternating tendency of monomer units in copolymer chain decreased. It is believed that the solvent polarity raises the reactivities of acrylonitrile monomer and its growing chain radical, but causes no distinct variation in those of 5-hexenoic acid.

Recently, many papers^[1-10] have been published on the effects of solvents on the reactivities of monomers in free radical copolymerization. Most works, however, were concerned with polar conjugated monomer pairs only, the pairs combined by weakly polar unconjugated and polar conjugated monomer have received little attention. In this paper the effects of solvent polarity on the behaviours of free radical copolymerization of 5-hexenoic acid (HA, M_1 ; a weakly polar unconjugated monomer) and acrylonitrile (AN, M_2 ; a polar conjugated monomer) were reported. Dimethylsulfone (DMSO), dimethylacetamide (DMA), dimethylformamide (DMF), cyclohexanone (CHN), and acrylonitrile were used as solvents. It was found that as the solvent polarity enhanced, both the copolymerization rate and the reactivity ratios r_1 , r_2 increased, while the alternating tendency of monomer units in copolymer molecular chain decreased. These experimental facts were discussed with IR spectral data and kinetic data, and mathematical analysis of Alfrey-Price equation.

EXPERIMENTAL

Materials

5-Hexenoic acid was prepared according to the method described in literature [11]. Acrylonitrile and the initiator 2,2'-azobisisobutyronitrile (AIBN) were purified by conventional methods. All solvents were treated by dehydration and redistilled prior to use.

Copolymerization

The given amounts of initiator, monomers and solvent were added into glass tubes, degassed by successive free-pump-thaw cycles, and then sealed under nitrogen atmosphere. Copolymerization was carried out at $60 \pm 0.1^\circ\text{C}$ and kept the conversion below 10%. Monomer concentration was 5 mol/liter except for bulk copolymerization (i.e. AN as solvent) in which monomer content was 0.025 mole. Initiator concentration was 0.5 mol% of the total monomers.

Table 1 Copolymerization of HA with AN in different polar solvents (60°C)

Solvent	Conversion wt%	Monomer feed		Copolymer composition		
		$X = \frac{[M_1]}{[M_2]}$	$f_1 = \frac{[M_1]}{[M_1] + [M_2]}$	N%	$Y = \frac{d[M_1]}{d[M_2]}$	$F_1 = \frac{d[M_1]}{d[M_1] + d[M_2]}$
DMSO	4.20	0.4288	0.3001	21.82	0.0975	0.0889
	6.24	0.8093	0.4473	18.96	0.1823	0.1542
	8.20	0.8234	0.4516	19.21	0.1740	0.1482
	3.86	1.2173	0.5490	17.11	0.2523	0.2015
	6.53	2.3311	0.6998	13.97	0.4136	0.2926
	7.86	4.0020	0.8001	11.16	0.6348	0.3883
DMA	4.73	1.8301	0.6467	16.63	0.3756	0.2731
	4.27	1.5038	0.6006	17.36	0.3193	0.2420
	4.41	0.9998	0.4999	18.94	0.2238	0.1829
	4.99	1.5050	0.6008	17.35	0.3203	0.2426
	6.42	1.8339	0.6471	16.69	0.3702	0.2702
	2.83	2.2855	0.6956	15.94	0.4387	0.3049
	2.90	2.9074	0.7441	15.25	0.515	0.3399
DMF	5.64	0.8164	0.4495	17.94	0.2192	0.1798
	3.65	0.8179	0.4499	18.25	0.2076	0.1719
	/	0.9958	0.4990	17.15	0.2507	0.2004
	0.84	0.9925	0.4981	17.21	0.2482	0.1989
	2.94	1.2396	0.5535	16.30	0.2880	0.2236
	1.87	1.8369	0.6475	14.06	0.4079	0.2897
	4.96	2.3047	0.6974	13.01	0.4784	0.3196
	2.86	2.3439	0.7009	13.13	0.4697	0.3236
AN* (bulk)	3.38	0.8154	0.4492	16.63	0.2595	0.2061
	2.81	1.5242	0.6038	14.02	0.4148	0.2932
	7.70	1.8290	0.6465	13.04	0.4765	0.3313
	2.57	2.3253	0.6993	12.23	0.5385	0.3500
	4.68	2.9737	0.7483	11.26	0.6250	0.3846
CHN	4.98	0.3217	0.2433	21.34	0.1099	0.0990
	4.10	0.4297	0.3005	21.01	0.1189	0.1063
	2.84	0.6681	0.4005	18.78	0.1882	0.1584
	3.30	0.6610	0.3980	19.12	0.1766	0.1501
	12.30	1.0101	0.5026	17.08	0.2533	0.2021
	8.30	3.5798	0.7817	11.09	0.6411	0.3907
	7.50	4.4010	0.8148	10.32	0.7236	0.4198

Conditions: $[M_1] + [M_2] = 5 \text{ mol/l}$, $[AIBN] = 0.5 \text{ mol\%}$

*: $[M_1] + [M_2] = 0.05 \text{ mol}$, $[AIBN] = 0.3 \text{ mol\%}$ (relative to monomers)

The above reaction mixture was poured into distilled-water to precipitate the polymer and the product was washed four times with water again, then dried in vacuum at 50°C for 48 hours.

Measurements

Copolymer compositions were calculated from N% in elemental analysis, using Elemental Analyzer Model-1160.

The IR spectra of HA and AN monomer in various solvents were recorded in liquid film at room temperature, a Nicolet MX-1 IR spectrometer was used.

RESULTS AND DISCUSSION

1. Effects of solvent polarity on monomer reactivities and sequences in copolymer chains

The compositions (as mole fraction) of the copolymers obtained in copolymerization of HA and AN in different solvents were shown in Table 1.

From these data, r_1 and r_2 were calculated by computer based upon the method of nonlinear least squares (Tidwell-Mortimer method⁽¹²⁾). The values of r_1 , r_2 and the corresponding solvent dielectric constants are given in Table 2.

Table 2 Reactivity ratios of monomers in different polar solvent

Solvent	r_1	r_2	$r_1 \cdot r_2$	μ	ϵ
DMSO	0.067	4.054	0.272	3.90	46.6
DMA	0.057	3.625	0.207	3.72	37.8
DMF	0.058	3.230	0.188	3.86	36.7
AN	0.054	3.107	0.167	3.51	33.0
CHN	0.044	2.362	0.104	3.01	18.3

μ : dipole moment of solvent (Debye)

ϵ : dielectric constant of solvent

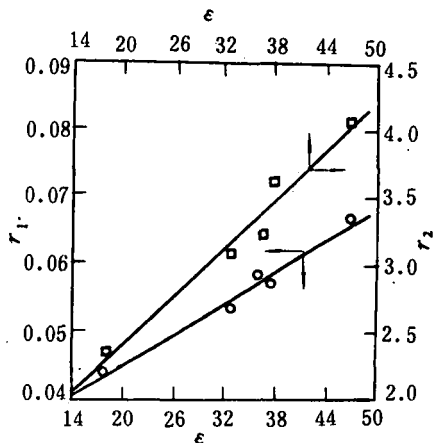


Fig. 1 The linear relationship between r_1 , r_2 and dielectric constant of solvents ϵ

Data in Table 2 indicate that the enhancement of solvent polarity results in increasing both r_1 and r_2 , while r_2 is more sensitive to polarity of solvents than r_1 . Furthermore, there is an approximately linear relation between monomer reactivity ratios and solvent polarity expressed as dielectric constants, as shown in Fig. 1.

Table 3 Sequence factors of copolymer calculated from reactivity ratios and monomer feeds X

Solvent	X	$\overline{L_n(M_1)}$	$\overline{L_n(M_2)}$	R
DMSO	0.429	1.03	10.4	17.4
	1.000	1.07	5.05	32.7
	2.333	1.16	2.74	51.4
DMA	0.429	1.02	9.45	19.1
	1.000	1.06	4.63	35.2
	2.333	1.13	2.55	54.2
DMF	0.429	1.02	8.53	20.9
	1.000	1.06	4.23	37.8
	2.333	1.14	2.38	56.8
AN	0.429	1.02	8.24	21.6
	1.000	1.05	4.11	38.8
	2.333	1.13	2.33	57.9
CHN	0.429	1.02	6.51	26.6
	1.000	1.04	3.36	45.4
	2.333	1.10	2.01	64.2

$$\overline{L_n(M_1)} = 1 + r_1 X, \overline{L_n(M_2)} = 1 + r_2/X, R = 200/(2 + r_1 X + r_2/X)$$

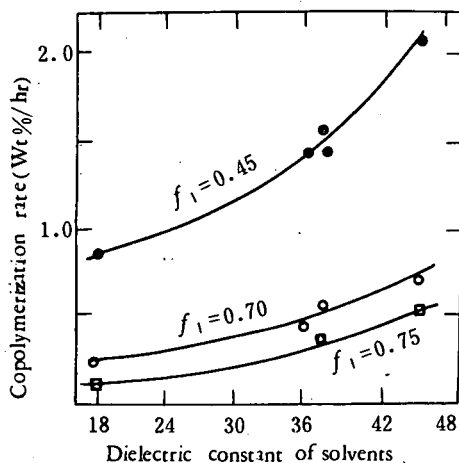


Fig. 2 The effect of solvent polarity on copolymerization rate with several monomer feeds f_1

The chain sequence distribution was determined from reactivity ratios of monomers by classical statistics^[13]. For copolymers prepared in various solvents from different monomer feed ratios X , number-average sequence lengths $\overline{L}_n(M_i)$ ($i = 1, 2$) and Harwood run numbers R (a parameter characterizing number-average alternating frequencies per hundred monomer units) were calculated, as shown in Table 3. It can be seen that with the same X , the chain sequence length of monomers $\overline{L}_n(M_1)$ and $\overline{L}_n(M_2)$ all increased and R decreased as the solvent polarity enhanced. The findings suggested that under these conditions, both M_1 - and M_2 -ending chains had a tendency to lengthen their own, and at the same time the chain alternating was declined.

2. Effects of solvent polarity on copolymerization rate

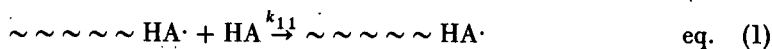
The correlations between solvent polarity and copolymerization rate with several monomer feeds f_1 are shown in Fig. 2. With the same monomer feed, the higher the solvent polarity, the greater the copolymerization rate; on the other hand, as the mole fraction of HA in monomer feed increases, the effect of solvent polarity on copolymerization rate becomes less markedly (the curve tends to be levelled off). This fact implies again that the influence of solvent polarity on reactivity of AN is more obvious than on HA.

3. Explanation of effects of solvent polarity on reactivity ratios of monomers

The influences of solvent polarity on polymer composition, chain sequence distribution and reaction rate reflect the effects of solvent polarity on reactivities of HA and AN monomer and their growing chain radicals, in one word, on monomer reactivity ratios. It implies that, on viewpoints of kinetics there are some variations in the ratio k_{ii}/k_{ij} , where k_{ii} and k_{ij} are the rate constants for the addition of i and j monomer to growing chain radical i , respectively.

It is known that the homopolymerization rate constants k_{22} of acrylonitrile at 60°C in DMSO ($\epsilon = 46.6$) and in DMF ($\epsilon = 36.71$) are $11600 \text{ l} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$ and $1960 \text{ l} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$, respectively^[14], hence, according to the definition of reactivity ratios and from the data for r_2 in Table 2, the cross chain propagating rate constants will be $k_{21} = k_{22}/r_2 = 2861 \text{ l} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$ in DMSO and $k_{21} = k_{22}/r_2 = 607 \text{ l} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$ in DMF, respectively. Thus, it is evident that both k_{22} and k_{21} increase with the increase of solvent polarity but k_{22} increases more markedly.

In the four steps of chain propagating reaction:



the enhancement of rate constants may be caused by the increase of reactivity of chain radical and/or monomers. For instance, the enhancements of HA monomer and/or $\sim \sim \text{AN} \cdot$ radical reactivity in polar solvents may lead to increasing k_{21} .

The IR spectral data of HA and AN monomers in different solvents are listed in Table 4. If the polarity of solvents influence the reactivities of the monomers, a corresponding change in the stretching frequency of carbon-carbon double bond should be observed. In fact, the stretching frequencies of C = C bond of HA monomer remain nearly unchanged in all solvents. Therefore, solvent polarity should have no effect on its reactivity, and the enhancement of k_{21} in eq. (3) should have to be attributed to the increase of reactivity in acrylonitrile chain radical. The increase of stretching frequencies of C = C bond in AN monomer with the increase of solvent polarity indicates that solvent polarity really has an influence on the reactivity of AN monomer as mentioned above, and enhances the reactivity of AN monomer too, resulting in a larger increase of the constant k_{22} than that of k_{21} . Fig. 3 shows a good linear relation between the stretching frequencies of C = C bond in AN monomer and $\log r_2$.

Table 4 IR stretching frequencies (cm^{-1}) of C = C and C $\equiv$ N groups of monomers in polar solvents

Monomer	Group	DMSO	DMA	DMF	AN	CHN	HA
HA	C = C	1641	1640	1651	-	1641	1642
AN	C = C	1606	1607	1608	1609	1610	-
	C $\equiv$ N	2229	2229	2229	2229	2230	-

Concentration of monomer: 5 mol/l, liquid film, room temperature

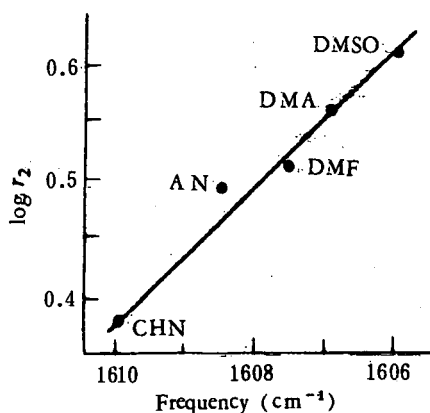
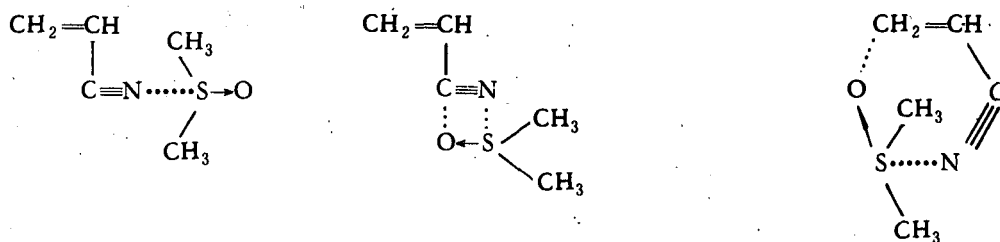


Fig. 3 The relation between stretching frequencies of C = C group in AN and $\log r_2$

The dipole association between solvent and nitrile group of AN may play an important role in enhancing AN reactivity. There are three types of interaction mechanisms shown in Scheme 1.

If two or six-central-point-interaction mechanism were true, the stretching frequencies of C $\equiv$ N group would be obviously different from each other in different solvents, because the vibrating directions of C $\equiv$ N group and that of the associated complexes are the same. If the four-central-point-interaction mechanism is the case, the stretching frequencies of C $\equiv$ N group in different polar solvents would not vary nearly. Data in Table 4 show no clear-cut change for the stretching frequencies of C $\equiv$ N group when solvent polarity varied. Thus the four-central-point-interaction mechanism is considered to be the most possible.



Two-centralpoint-interaction

Four-centralpoint-interaction

Six-centralpoint-interaction

Scheme 1

From consideration of structures of the monomers, it is known that HA with an electron-donor alkyl group is a weakly polar and unconjugated monomer, and that AN with an electron-withdrawing nitrile group is a strongly polar conjugated one. The manners and results of the monomers and their correlative growing chain radicals affected by solvent polarity should be different. In fact, however, both reactivity ratios of monomers all increase with the increase of solvent polarity.

According to Alfrey-Price equation:

$$r_1 = Q_1/Q_2 \cdot \exp[-e_1^*(e_1 - e_2)] \quad \text{eq. (5)}$$

where Q is conjugation factor of monomer, e and e^* are electrostatic factors of monomer and growing chain radical, respectively, a derivative of r_1 with respect to solvent polar parameter ϵ or μ can be deduced. Under the preconditions: $dQ_2/d\epsilon > 0$, $de_2/d\epsilon < 0$ ^[9,15], $dQ_1/d\epsilon = de_1/d\epsilon = 0$, i.e. no effect of solvent polarity on reactivity of HA monomer, and $dr_1/d\epsilon > 0$, i.e. r_1 increases with the increase of solvent polarity, an inequality can be deduced, and discussed as follows:

$$\frac{de_1^*/d\epsilon > \frac{e_1^*}{e_1 - e_2} de_2/d\epsilon}{(e_1 < e_2)} \quad \text{eq. (6)}$$

If $de_1^*/d\epsilon > 0$, then $e_1^* > 0$. It means that the HA growing chain radical possesses partial positive charge which will be enhanced with the increase of solvent polarity. It is evident that the reactivity of HA growing chain radical with AN monomer possessing partial negative charge will be increased. That is, the k_{12} in eq. (2) will decrease and k_{11} in eq. (1) will increase, so they make r_1 increase. The lowering of k_{12} means that the alternation of monomer units in polymer chain will be dropped. These appear to coincide with the experiments. But practically, from the viewpoints of organic chemistry theories and practices it is impossible that HA monomer carries partial negative charge and HA chain radical loads partial positive charge.

If $de_1^*/d\epsilon = 0$, then $e_1^* < 0$. In this case, both HA monomer and its growing chain radical should not be influenced by polarity of solvents, and the radical still possesses partial negative charge. Thus, k_{11} will be kept constant. But because the partial positive charge of AN monomer is reduced with the increase of solvent polarity ($de_2/d\epsilon < 0$), the reactivity of HA chain radical with AN monomer will be lowered, that is, k_{12} will be decreased. As a result, r_1 will increase and the alternating tendency of monomer units in polymer chain will decrease.

If $de_1^*/d\varepsilon < 0$, then $e_1^* < 0$, but $e_1^* \neq e_1$. It means that the HA growing chain radical carries partial negative charge which will be more negative with the increase of solvent polarity. The reactivity of the radical with HA monomer carrying partial negative charge will thus be lowered more obviously, so does k_{11} . Consequently, r_1 would not increase with the increasing solvent polarity unless k_{12} is decreased rather more with the increase of solvent polarity. This has to require inequality $|de_2/d\varepsilon| \gg |de_1^*/d\varepsilon|$ to be true. In general, it is impossible because of $de_2/d\varepsilon$ itself being very small.

Finally, it can be summarized that 1) the reactivity of HA monomer and its growing chain radical are not obviously affected by solvent polarity; 2) the main cause of r_1 increase may be that the solvent polarity reduces the partial positive charge at carbon-carbon double bond of AN monomer, resulting in decrease of its activity with HA chain radical holding partial negative charge.

It should be pointed out that reactivity ratios r_1 and stretching frequencies of C = C bond of HA are abnormal more or less when DMF used as solvent. Further experiments confirmed that this is due to the impurities, such as water, ammonia, etc..

Keywords: Copolymerization reactivities; Solvent polarity; Poly (5-hexenoic acid-co-acrylonitrile); Mathematical analyse Q-e scheme

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