

Hydrogen-bond-assisted syndiotactic-specific radical polymerization of *N*-isopropylacrylamide: the solvent effect on the stereospecificity

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Abstract

Radical polymerizations of *N*-isopropylacrylamide (NIPAAm) in several solvents at low temperatures in the absence or presence of hexamethylphosphoramide (HMPA) or 3-methyl-3-pentanol (3Me3PenOH) were examined. The isotacticities of the poly(NIPAAm)s obtained in the absence of HMPA and 3Me3PenOH at lower temperatures slightly increased as the polarities of the solvents used increased. The addition of HMPA significantly induced the syndiotactic-specificity even in polar solvents such as tetrahydrofuran and acetone, although the use of the solvents having proton-donating ability, such as chloroform, prevented the induction of the syndiotactic-specificity, even if their polarities are low. In the presence of 3Me3PenOH, a good correlation between the polarities of the solvents used and the syndiotacticities of

the obtained poly(NIPAAm)s was observed, and poly(NIPAAm) with $r = 73\%$ was obtained using the toluene/methylcyclohexane mixed solvent.

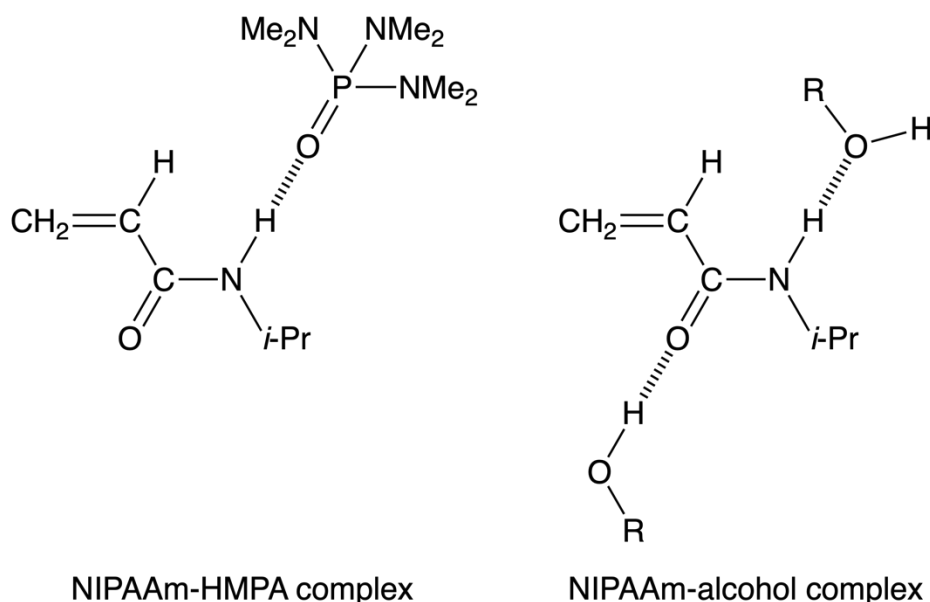
Keywords: hydrogen bond; *N*-isopropylacrylamide; syndiotactic-specific radical polymerization; solvent effect

1. Introduction

Poly(*N*-isopropylacrylamide) [poly(NIPAAm)] is one of the most attractive polymeric materials from both academic and industrial viewpoints, because of its stimuli-responsive character [1-2]. Radical copolymerizations of NIPAAm with other monomers have been extensively studied to control the stimuli-responsiveness [3]. However, although the stereostructure of macromolecules also significantly influences polymer properties, there are limited reports on stereoregularity of poly(NIPAAm) [4-7].

Recently, we have reported the hydrogen-bond-assisted stereospecific radical polymerizations of NIPAAm, in which Lewis bases (LBs) [8-15] and alcohol compounds [16,17] play important roles as stereocontrolling auxiliaries. For example, the addition of hexamethylphosphoramide (HMPA) into the NIPAAm polymerizations in toluene at -60°C afforded poly(NIPAAm) with *racemo* (r) dyad content of 72% [10]. The NMR analysis suggested that complex formation between NIPAAm monomer and HMPA through a hydrogen-bonding interaction ($\text{N-H} \cdots \text{O}=\text{P}$) is responsible for the induction of the syndiotactic-specificity [9]. Furthermore, the addition of 3-methyl-3-pentanol (3Me3PenOH) into the NIPAAm polymerizations in toluene at -60°C also afforded

poly(NIPAAm) with $r = 71\%$ [16]. In this polymerization, it was revealed that the added alcohols formed hydrogen-bonding interaction not only with N-H group but also with C=O group of NIPAAm monomer. Thus, it is assumed that the syndiotactic-specificities induced by HMPA and 3Me3PenOH could be tuned by changing the polarity of the polymerization system. In this study, we examined the effect of solvents on the stereospecificities of the NIPAAm polymerizations at low temperatures.



2. Experimental

2.1. Materials

NIPAAm (Tokyo Kasei Kogyo Co.) was recrystallized from hexane-benzene mixture. Chloroform, tetrahydrofuran (THF) and acetonitrile (Wako Co.) were fractionally distilled before use. Tri-*n*-butylborane (*n*-Bu₃B) as a THF solution (1.0M), HMPA (Aldrich Chemical Co.), 3Me3PenOH (Tokyo Kasei Kogyo Co.), dichloromethane, and acetone (Wako Co.) were used without further purification for polymerization reactions.

2.2. Polymerization

Typical polymerization procedure is as follows; NIPAAm (0.628 g, 5.5 mmol) was dissolved in CHCl_3 to prepare the 5 mL solution of 1.1 mol/L. Four milliliter of the solution was transferred to the glass ampoule and cooled at the desired temperature. The polymerization was initiated by adding $n\text{-Bu}_3\text{B}$ solution (0.44 mL) into the monomer solution under air [18]. After 24h, the reaction was terminated with a small amount of THF solution of 2,6-di-*t*-butyl-4-methylphenol at polymerization temperature. The polymerization mixture was poured into a large amount of diethyl ether, and the precipitated polymer was collected by filtration or centrifugation, and dried *in vacuo*. The polymer yield was determined gravimetrically.

2.3. Measurements

The ^1H NMR spectra were measured on an EX-400 spectrometer (JEOL Ltd.) operated at 400MHz. The tacticities of the obtained poly(NIPAAm)s were determined from ^1H NMR signals due to methylene group in main chain, measured in deuterated dimethyl sulfoxide ($\text{DMSO-}d_6$) at 150°C. The ^1H NMR spectra of CHCl_3 , CH_2Cl_2 , acetone, and CH_3CN (0.20 mol/L), respectively, in the absence or presence of equimolar amounts of HMPA or 3Me3PenOH (0.20 mol/L) were measured in toluene- d_8 at 25°C. The molecular weights and molecular weight distributions of the polymers were determined by size exclusion chromatography (SEC) (HLC 8220 instrument (Tosoh Co.)) equipped with TSK gels (SuperHM-M and SuperHM-H (Tosoh Co.)) using

dimethylformamide (LiBr 10 mmol/L) as an eluent at 40°C ([polymer] = 1.0 mg/mL, flow rate = 0.35 mL/min). The SEC chromatogram was calibrated with standard polystyrene samples.

3. Results and Discussion

3.1. Solvent effect on the stereospecificity in the radical polymerization of NIPAAm in the absence of syndiotactic-specificity-inducers

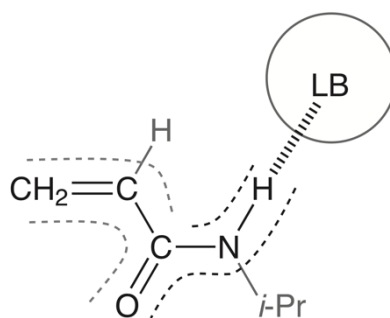
We first investigated the solvent effect on the stereospecificity in the radical polymerization of NIPAAm in the absence of syndiotactic-specificity-inducers such as HMPA and 3Me3PenOH (Table 1). The tacticities of the obtained polymers at 0°C were independent of the polarities of the solvents used, except for CH₃CN (55% ± 2%). The *r* dyad content, however, gradually decreased with a decrease in the polymerization temperature, as the polarities of the solvents used increased. In particular, the use of CH₃CN enhanced such tendency and *m* dyad content reached to 57% by lowering the temperature to -40°C. Similar solvent effects have been reported for the radical polymerization of *N,N*-disubstituted acrylamide [19] and fluoroalkyl acrylates [20].

<Table 1>

3.2. Solvent effect on the syndiotactic-specificity in the radical polymerization of NIPAAm in the presence of HMPA

Table 2 summarizes the results of the radical polymerization of NIPAAm in

various solvents at low temperatures in the presence of HMPA. The molecular weights of the obtained polymers decreased with the addition of HMPA, regardless of the solvents used except for CHCl_3 . As previously reported [15,16], complex formation between NIPAAm monomer and LBs would reduce the polymerizability of NIPAAm monomer, because of the cross-conjugation structure of NIPAAm monomer. Thus, the decreases in the molecular weights suggest that HMPA worked as the syndiotactic-specificity-inducer in the solvents, except for CHCl_3 .



<Table 2>

The polymer with r dyad content of 70% were obtained in the toluene/methylcyclohexane mixed solvent at -40°C , whereas radical polymerization in toluene required lowering the temperature to -60°C to obtain the polymer with $r = 70\%$. It was probably because less polarity of the mixed solvent enhanced the hydrogen-bonding interaction between NIPAAm and HMPA. However, the syndiotacticity decreased by further lowering the temperature. As mentioned above, the complex formation would reduce the polymerizability of the NIPAAm monomer. Thus, it

is assumed that the incorporation of non-stereospecific free monomers, which have polymerizability higher than the complexed monomers, into propagation steps increased at lower temperatures, although the concentration of the free monomer should be quite low.

The use of THF and acetone as solvents afforded the polymers, of which *r* dyad contents were as high as those of the polymers obtained in toluene; the polymers with *r* dyad contents of 79% and 75% were obtained in THF and acetone, respectively, at -60°C . These results indicate that HMPA can induce the significant syndiotactic-specificity even in polar media such as THF and acetone.

Fig. 1 shows the relationship between the dielectric constant of the solvents used and the *r* dyad contents of poly(NIPAAm)s prepared at -40°C in the presence of HMPA. A correlation between the polarities of the solvents and the *r* dyad content of the obtained polymers seems to be found in the plots for the toluene/methylcyclohexane mixed solvent, toluene, THF, and acetone. Interestingly, the plots for CHCl_3 , CH_2Cl_2 , and CH_3CN obviously deviated from the correlation. It is known that these solvents form hydrogen-bonding interaction with LBs [21-27]. In fact, a downfield shift was clearly observed in ^1H NMR signals of CHCl_3 , CH_2Cl_2 , and CH_3CN by adding an equimolar amount of HMPA [28], whereas the signal of acetone hardly changed (Table 3). This means that HMPA forms the hydrogen bond with these solvents as well as with NIPAAm. Thus, it is concluded that not only the polarities of the solvents but also the hydrogen-bonding interaction between HMPA and the solvents are important factors in the HMPA-mediated syndiotactic-specific radical polymerization of NIPAAm.

<Fig. 1>

<Table 3>

3.3. Solvent effect on the syndiotactic-specificity in the radical polymerization in the presence of 3Me3PenOH

The solvent effect on the syndiotactic-specificity in NIPAAm polymerization in the presence of 3Me3PenOH was examined (Table 4). In contrast with the HMPA-mediated polymerizations, the molecular weights of the obtained polymers increased as compared with those obtained in the absence of the syndiotactic-specificity-inducers, although the NIPAAm monomer was used at a half concentration. Further, the tendency was enhanced as the polarities of the solvents used decreased. Taking into account that hydrogen bond formation between C=O and –OH significantly enhances k_p in radical polymerization of α,β -unsaturated ester monomers [29-31], it was suggested that 3Me3PenOH worked as the syndiotactic-specificity-inducer even in the solvents other than toluene.

<Table 4>

In fact, syndiotactic-rich polymers were obtained by the radical polymerization in all the solvents examined in this study. The effectiveness of 3Me3PenOH as the syndiotactic-specificity-inducer depended on the polarities of the solvents used. In

particular, the use of the toluene/methylcyclohexane mixed solvent at -70°C and -60°C afforded the poly(NIPAAm)s with $r = 73\%$, the highest syndiotacticity value of radically prepared poly(NIPAAm)s.

Fig. 2 displays the relationship between the dielectric constants of the solvents used and the r dyad contents of poly(NIPAAm)s obtained at -40°C in the presence of 3Me3PenOH. The plots exhibited a good correlation, except for those in CHCl_3 and THF. It is known that CHCl_3 forms $\text{C-H} \cdots \text{O}$ hydrogen bond even with alcohols [32,33]. In fact, a slight downfield shift was observed in ^1H NMR signal of CHCl_3 by adding an equimolar amount of 3Me3PenOH, whereas a downfield shift was hardly observed in those of CH_2Cl_2 (*cf.* Table 3). On the other hand, it is also well known that THF forms $\text{O} \cdots \text{H-O}$ hydrogen bond with alcohols [34-36]. Thus, it is assumed that the complex formation between the solvent used and 3Me3PenOH reduced the induced syndiotactic-specificity, although the influence of the complexation was much smaller than that in the HMPA-mediated polymerizations.

<Fig. 2>

4. Conclusions

It was found that the polarities of the solvents used affected the stereospecificity of NIPAAm polymerization even in the absence of HMPA and 3Me3PenOH. In particular, the use of CH_3CN as a solvent afforded poly(NIPAAm)s rich in m dyad. The addition of HMPA significantly induced the syndiotactic-specificity even

in polar solvents such as THF and acetone. However, the used solvents, which have proton-donating ability, reduced the syndiotactic-specificity induced by HMPA. A good correlation between the polarities of the solvents and the syndiotacticity of the poly(NIPAAm)s obtained in the presence of 3Me3PenOH was observed. The use of the toluene/methylcyclohexane mixed solvent resulted in the formation of poly(NIPAAm)s with $r = 73\%$. Further work is in progress to examine the effect of the *N*-substituents on the syndiotactic-specificity induced by HMPA and 3Me3PenOH.

Acknowledgement.

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Table 1.

Radical polymerization of NIPAAm in various solvents for 24h at low temperatures in the absence of syndiotactic-specificity-inducers

Run	Solvent	Temp. °C	Yield %	Tacticity / % ^a		M_n^b x 10 ⁻⁴	M_w^b M_n
				<i>m</i>	<i>r</i>		
1 ^{c,d}	Toluene	0	>99	45	55	7.0	1.9
2 ^{c,d}	Toluene	-20	56	45	55	3.4	2.3
3 ^{c,d}	Toluene	-40	84	44	56	1.6	2.0
4 ^{c,d}	Toluene	-60	10	43	57	0.7	1.8
5 ^{c,d}	Toluene	-80	18	44	56	1.1	3.5
6 ^d	Tol + MeCy ^e	0	99	47	53	5.0	3.1
7 ^d	Tol + MeCy ^e	-20	96	46	54	4.4	3.1
8 ^d	Tol + MeCy ^e	-40	93	47	53	3.4	3.6
9 ^d	Tol + MeCy ^e	-60	79	48	52	5.2	2.8
10 ^d	Tol + MeCy ^e	-80	54	47	53	4.2	3.8
11	CHCl ₃	0	>99	46	54	1.5	1.6
12	CHCl ₃	-20	96	45	55	1.9	1.6
13	CHCl ₃	-40	88	47	53	1.0	2.0
14 ^d	CHCl ₃	-60	30	48	52	0.8	2.0
15	THF	0	68	43	57	1.6	1.5
16	THF	-20	82	45	55	1.9	1.5
17	THF	-40	55	48	52	2.1	1.7
18	THF	-60	32	50	50	1.8	1.7
19	CH ₂ Cl ₂	0	>99	44	56	2.7	1.7
20	CH ₂ Cl ₂	-20	>99	46	54	3.3	1.6
21	CH ₂ Cl ₂	-40	81	47	53	3.6	1.7
22	CH ₂ Cl ₂	-60	65	51	49	2.9	2.1
23	Acetone	0	63	46	54	2.8	2.9
24	Acetone	-20	56	49	51	2.6	2.6
25	Acetone	-40	44	52	48	2.7	3.9
26	Acetone	-60	20	55	45	1.8	2.4
27	CH ₃ CN	0	93	49	51	3.3	2.1
28	CH ₃ CN	-20	99	53	47	3.9	2.0
29	CH ₃ CN	-40	>99	57	43	2.7	2.9

[NIPAAm]₀ = 1.0 mol/L, [*n*-Bu₃B]₀ = 0.10 mol/L.

a. Determined by ¹H NMR signals due to methylene group.

b. Determined by SEC (polystyrene standards).

c. Data taken from Ref. [9].

d. Monomer, polymer or both were precipitated during a polymerization reaction.

e. Mixed solvent: toluene / methylcyclohexane (1:1 vol/vol).

Table 2.

Radical polymerization of NIPAAm in various solvents for 24h at low temperatures in the presence of HMPA

Run	Solvent	Temp. °C	Yield %	Tacticity / % ^a		M_n^b x 10 ⁻⁴	M_w^b M_n
				<i>m</i>	<i>r</i>		
1 ^c	Toluene	0	98	37	63	0.9	1.6
2 ^c	Toluene	-20	>99	34	66	1.0	1.7
3 ^c	Toluene	-40	99	32	68	1.3	2.2
4 ^c	Toluene	-60	>99	30	70	1.0	1.9
5 ^c	Toluene	-80	86	36	64	1.3	1.6
6	Tol + MeCy ^e	0	54	34	66	1.6	1.3
7	Tol + MeCy ^e	-20	80	32	68	1.7	1.5
8	Tol + MeCy ^e	-40	89	30	70	2.0	2.8
9 ^d	Tol + MeCy ^e	-60	>99	32	68	2.5	2.8
10 ^d	Tol + MeCy ^e	-80	91	42	58	2.1	2.3
11	CHCl ₃	0	89	43	57	1.4	1.7
12	CHCl ₃	-20	>99	44	56	2.8	2.1
13	CHCl ₃	-40	66	45	55	5.1	2.2
14 ^d	CHCl ₃	-60	>99	47	53	2.2	2.2
15	THF	0	63	37	63	0.9	1.5
16	THF	-20	61	34	66	1.0	1.6
17	THF	-40	69	33	67	1.7	1.5
18	THF	-60	81	31	69	1.3	1.8
19	CH ₂ Cl ₂	0	86	40	60	1.0	1.6
20	CH ₂ Cl ₂	-20	94	40	60	1.1	1.8
21	CH ₂ Cl ₂	-40	93	39	61	1.3	1.7
22	CH ₂ Cl ₂	-60	90	40	60	1.2	1.8
23	Acetone	0	71	38	62	0.9	1.7
24	Acetone	-20	69	37	63	0.9	1.6
25	Acetone	-40	84	35	65	1.2	1.8
26	Acetone	-60	91	35	65	1.1	2.0
27	CH ₃ CN	0	76	45	55	1.0	1.7
28	CH ₃ CN	-20	76	45	55	1.1	1.6
29	CH ₃ CN	-40	89	50	50	0.8	1.6

[NIPAAm]₀ = 1.0 mol/L, [*n*-Bu₃B]₀ = 0.10 mol/L, [HMPA]₀ = 2.0 mol/L.

a. Determined by ¹H NMR signals due to methylene group.

b. Determined by SEC (polystyrene standards).

c. Data taken from Ref. [9].

d. Monomer, polymer or both were precipitated during a polymerization reaction.

e. Mixed solvent: toluene / methylcyclohexane (1:1 vol/vol).

Table 3.

The ^1H NMR chemical shifts of CHCl_3 , CH_2Cl_2 , acetone, CH_3CN in toluene- d_8 at 25°C in the absence or presence of an equimolar amount of HMPA or 3Me3PenOH

	Chemical shift / ppm ^a		
	None	HMPA	3Me3PenOH
CHCl_3	6.10	7.08 (0.98)	6.19 (0.09)
CH_2Cl_2	4.30	4.54 (0.24)	4.33 (0.03)
acetone	1.59	1.63 (0.04)	nd ^b
CH_3CN	0.73	0.95 (0.22)	nd ^b

a. The values in parentheses are the changes in the chemical shifts with the addition of HMPA or 3Me3PenOH.

b. Not determined.

Table 4.

Radical polymerization of NIPAAm in various solvents for 24h at low temperatures in the presence of 3Me3PenOH

Run	Solvent	Temp. °C	Yield %	Tacticity / % ^a		M_n^b x 10 ⁻⁴	M_w^b M_n
				<i>m</i>	<i>r</i>		
1 ^c	Toluene	0	>99	36	64	5.5	1.4
2 ^c	Toluene	-20	>99	32	68	6.0	1.4
3 ^c	Toluene	-40	>99	31	69	5.9	1.5
4 ^{c,d}	Toluene	-60	>99	29	71	8.9	1.5
5 ^{c,d}	Toluene	-80	>99	30	70	8.2	1.5
6	MeCy + Tol ^e	0	90	35	65	5.7	1.7
7	MeCy + Tol ^e	-20	98	31	69	8.7	1.9
8	MeCy + Tol ^e	-40	90	29	71	6.2	1.9
9	MeCy + Tol ^e	-50	97	28	72	9.5	1.9
10	MeCy + Tol ^e	-60	88	27	73	5.5	2.5
11 ^d	MeCy + Tol ^e	-70	88	27	73	6.9	2.6
12 ^d	MeCy + Tol ^e	-80	57	28	72	20.5	2.2
13	CHCl ₃	0	90	41	59	2.3	1.7
14	CHCl ₃	-20	97	40	60	2.7	1.7
15	CHCl ₃	-40	95	38	62	4.8	1.7
16	CHCl ₃	-60	98	36	64	3.8	1.8
17	THF	0	61	41	59	2.1	1.3
18	THF	-20	67	39	61	2.2	1.3
19	THF	-40	65	38	62	3.0	1.3
20	THF	-60	70	37	63	3.3	1.4
21	CH ₂ Cl ₂	0	88	42	58	2.4	1.4
22	CH ₂ Cl ₂	-20	96	39	61	2.8	1.7
23	CH ₂ Cl ₂	-40	88	36	64	3.6	1.5
24 ^d	CH ₂ Cl ₂	-60	98	33	67	4.1	1.7
25 ^c	Acetone	0	33	43	57	2.0	1.3
26	Acetone	-20	51	41	59	2.1	1.3
27	Acetone	-40	52	39	61	3.0	1.4
28	Acetone	-60	69	37	63	4.6	1.6
29 ^d	CH ₃ CN	0	50	44	56	2.1	1.4
30 ^d	CH ₃ CN	-20	77	42	58	2.3	1.5
31 ^d	CH ₃ CN	-40	62	39	61	5.2	3.2

[NIPAAm]₀ = 0.5 mol/L, [*n*-Bu₃B]₀ = 0.05 mol/L, [3Me3PenOH]₀ = 2.0 mol/L.

a. Determined by ¹H NMR signals due to methylene group.

b. Determined by SEC (polystyrene standards).

c. Data taken from Ref. [16].

d. Monomer, polymer or both were precipitated during a polymerization reaction.

e. Mixed solvent: toluene / methylcyclohexane (1:1 vol/vol).

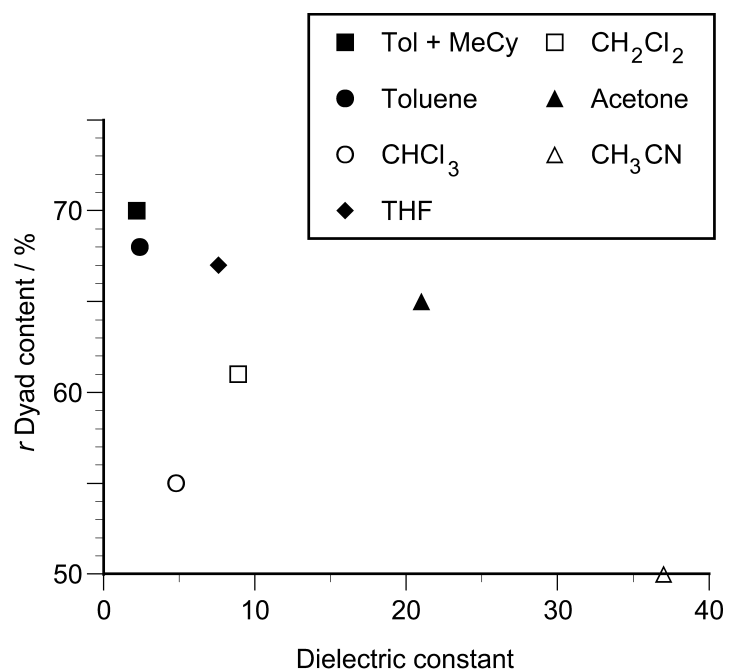


Fig. 1. The relationship between the dielectric constant of the solvents used and the *r* dyad contents of poly(NIPAAm)s prepared at -40°C in the presence of HMPA

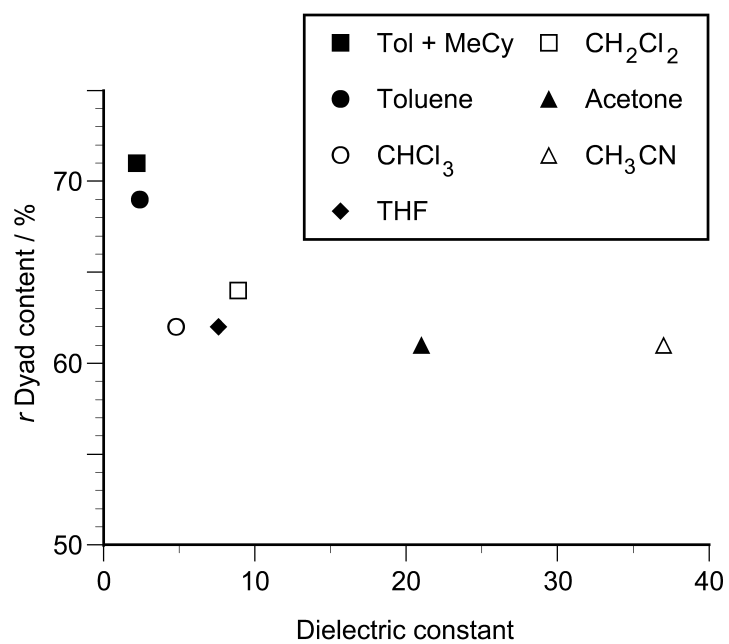


Fig. 2. The relationship between the dielectric constant of the solvents used and the *r* dyad contents of poly(NIPAAm)s prepared at -40°C in the presence of 3Me3PenOH