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Stereoregularity of poly(4-vinyl-n-alkyl-pyridinium) salts prepared by spontaneous polymerization

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Abstract

A series of poly(4-vinylpyridinium salts) was prepared by spontaneous polymerization of 4-vinylpyridine in the presence of various alkylating agents and at different temperatures in order to study by ^{1}H-NMR the stereoregularity of the obtained polysalts. Contrarily to poly(4-vinylpyridine) which always gives an atactic structure, the polysalts were found to have an isotactic character. The observed isotactic triad content varies from 30%–50% and increase when the temperature of the polymerization decreases and with the hydrophobic character of the side chain. The preferential isotactic placement is explained in terms of the zwitterionic polymerization mechanism and the formation of a sandwich-like association between a quaternized monomer and the growing chain, an association stabilized by Coulombic interactions.

Keywords: Poly(4-vinyl-N-alkyl-pyridinium salts); Spontaneous polymerization; Stereoregularity

1. Introduction

The spontaneous polymerization of 4-vinylpyridine upon quaternization or protonation to form the corresponding poly(4-vinylpyridinium salts) has been of considerable interest [1–6]. Recently this simple polymerization process was used to prepare a series of side-chain liquid crystalline polysalts by quaternization with mesogenic groups [7–9] and of electrolyte polymers by quaternization with short poly(ethylene oxide) chains [10]. The mechanism of this specific polymerization has been debated for a long time [2–4], and it is now well recognized that two methods of initiation exist. In the presence of a strong nucleophilic counterion, the initiation occurs by addition of the counterion or of 4-vinylpyridine to the β-position of the double bound of the 4-vinylpyridinium salt to yield a highly resonance-stabilized zwitterion [4]. The propagation occurs by nucleophilic addition to a 4-vinylpyridinium ion to continuously regenerate a zwitterionic endgroup. The termination step is the deactivation of the macromolecular chain by the alkyl agent. Nevertheless, in spite of the numerous studies done on the polymerization mechanism, no studies have been published on the stereoregularity of poly(4-vinylpyridinum salts) prepared by this process. As tacticity may also affect the properties of such materials, it is of interest to investigate this aspect.

In this article, various poly(4-vinylpyridinium salts) were prepared by spontaneous polymerization at different temperatures and using several types of alkylating agents, and their tacticities studied by means of ^{1}H-NMR spectroscopy.

2. Experimental part

All the solvents were distilled before use. 4-Vinylpyridine (Aldrich) was distilled under vacuum in the presence of KOH and hydroquinone. Methyl iodide, methyl chloride, 3-bromopropene, 1-bromooctane, benzyl bromide and vinyl benzyl chloride (mixture of 3- and 4 isomers) all from Aldrich were used without further purification. Bromo- and tosyl-triethylene glycol monomethyl ether was prepared from carefully distilled triethylene glycol monomethyl ether (Aldrich). The bromo derivative was prepared by reaction with thionyl bromide in toluene in the presence of pyridine. The tosyl derivative was prepared from tosyl chloride in CH_2Cl_2 in the presence of NEt_3. Both derivatves were purified by silica gel chromatography. Monochloro-triethylene glycol was prepared from distilled triethylene glycol (Aldrich) and tosyl chloride. The monochloro derivative was obtained by separation with silica gel chromatography.

Polymerizations were carried out in 4-vinylpyridine in

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Table 1
Preparation of poly(4-vinylpyridinium) salts by spontaneous polymerization using various alkylating agents and 4-vinylpyridine as solvent and reactant

Ref	Alkylating agent RX	Times (h)	*T* (°C)	[RX] mol/l	Yield (%)	$\overline{DPw}$	Coloration of medium
P1	CH_3I	1.25	20	1.34	90		yellow
P2	CH_3Cl	2.33	20	1.32	40		pink–red
P3	$CH_3\ (CH_2)_7\ Br$	1.25	50	1.33	25		claret
P4	$CH_3\ (OCH_2CH_2)_3\ Br$	120	50	0.82	76	600	blue–green
P5	$H(OCH_2CH_2)_3Cl$	120	50	0.82			red–orange
P6	$CH_3(OCH_2CH_2)_3Ots$	168	50	0.82	82		pink
P7	$C_6H_5CH_2Br$	24	20	1.20	90	77	red
P8	$C_6H_5CH_2Br$	24	0	1.20	90	89	red
P9	$C_6H_5CH_2Br$	24	− 5	1.20	90	137	red
P10	$C_6H_5CH_2Br$	24	− 16	1.20	90	221	red
P11	$C_6H_5CH_2Br$	24	− 30	1.20	90	373	red
P12	$CH_2{=}CHCH_2Br$	2	− 5	1.47	80		peach
P13	$CH_2{=}CHCH_2Br$	2	− 30	1.47	80		peach
P14	$CH_2{=}CH(C6H4)CH_2Cl$	144	25	1.00	76		red

sealed tubes after several outgassings as already described [7]. A small amount of hydroquinone was added to prevent the thermal polymerization of 4-vinylpyridine. As a general rule, polymers were recovered by repeated dissolution in methylene chloride and precipitation in diethyl ether. They were dried under vacuum at 40°C. Yields were calculated from the amount of alkylating agent introduced. The structure of these polymers was analyzed by ^1H NMR (Bruker 200 MHz) in $CDCl_3$ and by elemental analysis:

As already noted [7], both methods of analysis often demonstrate the presence of a half or one water molecule per pyridinium unit. However, products can be obtained in an anhydrous form by heating at 70°C in vacuum and keeping dry at room temperature. For polymers soluble in methanol, molecular weights were determined by light scattering in this solvent.

^1H-NMR tacticity measurements were carried out on a Bruker 200 MHz spectrometer. The spectra of the poly(4-vinylpyridinium salts) were determined in CDCl3 with a few drops of CD3OD. The amount of isotactic triads was obtained from the relative intensities of the methine and methylene protons of the backbone. The Pasc-Linesim software (Bruker) was used for peaks deconvolution. Molecular modeling was accomplished on a Silicon Graphics computer equipped with Sybyl software. Transmission IR spectra were recorded using a FTIR Bomem spectrophotometer.

3. Results and discussion

The poly(4-vinylpyridinium salts) were synthesized by spontaneous polymerization in sealed tubes at different

		%C	%H	%N	%S	%Cl	%Br
$P4VP^+CH_3,I^-$, 20°C	Calc	38.88	4.05	5.66			
	Fnd	35.28	4.35	5.11			
$P4VP^+(CH_2)_7CH_3,Br^-$, 50°C	Calc	60.40	8.11	4.70			
	Fnd	56.90	8.21	4.40			
$P4VP^+(CH_2CH_2O)_3CH_3,Br^-$, 50°C	Calc	50.61	6.67	4.22			24.05
	Fnd	50.43	7.09	4.17			22.35
$P4VP^+(CH_2CH_2O)_3CH_3,OTs^-$, 50°C	Calc	59.56	6.90	3.31	7.57		
	Fnd	59.35	7.19	3.41	5.59		
$P4VP^+CH_2(C_6H_5),Br^-$, 20°C	Calc	60.89	5.11	5.07			28.93
	fnd	57.20	5.50	4.79			27.14
$P4VP^+CH_2(C_6H_5), Br^-$, 0°C	Calc	60.89	5.11	5.07			28.93
	Fnd	57.18	5.46	4.78			27.16
$P4VP^+CH_2(C_6H_5), Br^-$, − 5°C	Calc	60.89	5.11	5.07			28.93
	Fnd	57.17	5.42	4.75			27.13
$P4VP^+\ CH_2(C_6H_5), Br^-$, − 16°C	Calc	60.89	5.11	5.07			28.93
	Fnd	57.13	5.50	4.74			27.10
$P4VP^+\ CH_2(C_6H_5), Br^-$, − 30°C	Calc	60.89	5.11	5.07			28.93
	Fnd	57.16	5.49	4.75			27.15
$P4VP^+CH_2CH = CH_2, Br^-$, − 30°C	Calc	53.09	5.31	6.19			
	Fnd	51.10	5.60	5.91			
$P4VP^+\ CH_2C_6H_5CH = CH_2, Cl^-$, − 25°C	Calc	74.56	6.26	5.43		13.75	
	Fnd	68.65	6.61	5.17		11.56	

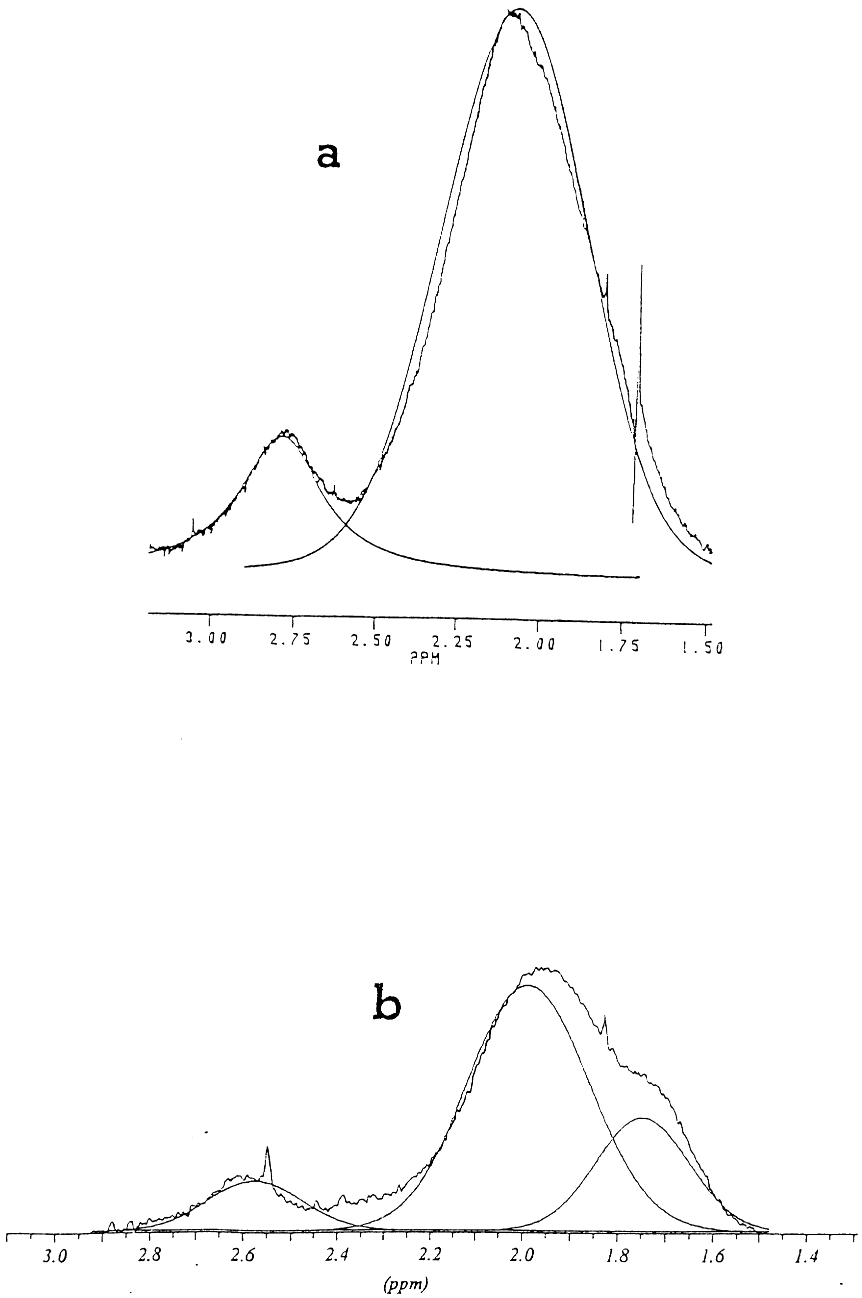

Fig. 1. ^{1}H NMR deconvolution of the main chain signals for the poly(4-vinyl-N-methyl pyridinium iodide)(P1) (a) and chloride (P2) (b).

temperatures using different alkylating agents and 4-vinylpyridine as solvent and reactant. Conditions of preparation and molecular weight analysis are summarized in Table 1. The polymerization media are colored because of a charge transfer band [11]. ^{1}H-NMR spectroscopy and elemental analysis demonstrate that the polysalts are totally quaternized. The spontaneous polymerization process allows high molecular weights to be obtained and the lower the polymerization temperature, the higher is the molecular weight as demonstrated by the samples P7 to P11. This behaviour is the result of a slower initiation reaction at the lower temperature.

Preliminary experiments demonstrated that quantitative analysis of the tacticity of the polysalts using ^{13}C NMR was not possible as already observed by Matsuzaki et al. [12] for poly(4-vinylpyridine) (P4VP). Indeed, C-4 in the pyridinium ring, normally sensitive to the stereoconfiguration, gave only one signal and methine and methylene carbon absorptions overlap each other. The ^{1}H NMR spectra of the polysalts were then measured and analyzed according to the method described by Matsuzaki et al. [12] for P4VP analysis. From the comparison of deuterated and non-deuterated P4VP samples, these authors showed that only a fraction of isotactic triad can be obtained from the ^{1}H NMR

Table 2
Isotactic triad content of polysalts obtained from the deconvolution of ^{1}H NMR spectra

Ref	Polysalts	T polym. (°C)	Isotactic triad content (mm) ±3%
P1	P4VP$^+$CH$_3$ I$^-$	20	0.297
P2	P4VP$^+$CH$_3$ Cl$^-$	20	0.306
P7	P4VP$^+$CH$_2$(C$_6$H$_5$), Br$^-$	20	0.405
P8	P4VP$^+$CH$_2$(C$_6$H$_5$), Br$^-$	0	0.423
P9	P4VP$^+$CH$_2$(C$_6$H$_5$), Br$^-$	−5	0.450
P10	P4VP$^+$CH$_2$(C$_6$H$_5$), Br$^-$	−16	0.480
P11	P4VP$^+$CH$_2$(C$_6$H$_5$), Br$^-$	−30	0.488
P12	P4VP$^+$CH$_2$CH=CH$_2$, Br$^-$	−5	0.436
P13	P4VP$^+$CH$_2$CH=CH$_2$, Br$^-$	−30	0.484
P14	P4VP$^+$CH$_2$(C6H4)CH=CH$_2$, Cl$^-$	20	0.490

spectra of non-deuterated P4VP. The spectra show that the methine proton absorption of heterotactic and syndiotactic triads completely overlaps the methylene proton absorption at 2.1 ppm. However, the methine proton absorption of the isotactic triad located at 2.8 ppm is well apart from the other absorptions and allows a quantitative analysis. A similar behaviour was observed for most of our poly(4-vinyl pyridinium) samples as shown in Fig. 1a. Only in one case (P2 sample), and without obvious reason, does the contribution of the proton absorption of the syndiotatic triad appear clearly as a shoulder around 1.75 ppm as shown in Fig. 1b.

Following Matsuzaki, the fraction of isotactic triad I is calculated according to Eq. (1):

$$I(\%) = 3A_I \times 100 \tag{1}$$

where A_I is the ratio of the lowest methine proton absorption to the sum of the methine and methylene proton absorptions.

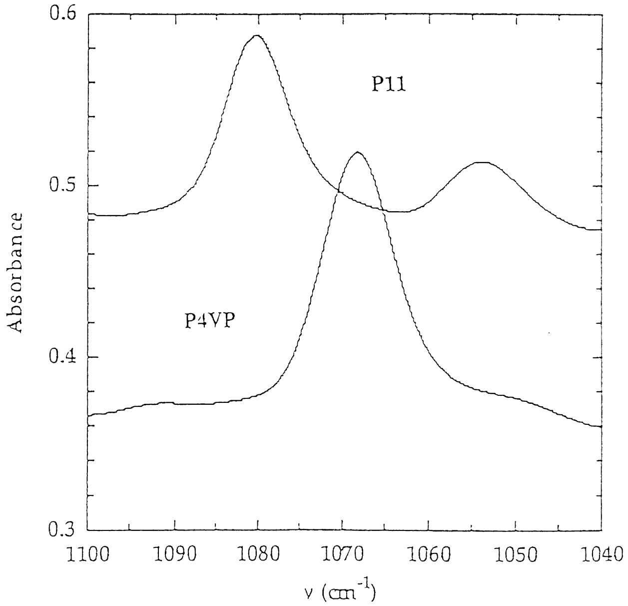

Fig. 2. FTIR spectra of an atactic poly(4-vinyl pyridine) and of poly(4-vinyl-N-benzylpyridinium bromide)(P11).

However, the determination of the isotactic triad content was not precise enough for all the samples for two main reasons. First, with tosylate anion or paraffin chains (P6 and P3) as substituent, the signals associated with their structures overlap with those of the polymer main chain in the studied region. Experiments with deuterated samples would be necessary. Second, with bromo-triethylene glycol monomethyl ether (P4) and monochloro-triethylene glycol (P5) alkylating agents, the ^{1}H NMR signals for the macromolecular chain were too broad to be useful. Nevertheless, for ten samples, the contents of isotactic triads could be determined with good precision. The results are gathered in Table 2. The polysalts show an isotactic triad content in the range 0.30–0.50, the content increasing with decrease in temperature. In order to underline the specific character of the spontaneous polymerization, the results may be compared with the isotactic triad contents of P4VP obtained by radical or anionic polymerization [12]. While poly(2-vinylpyridine) can be easily obtained with a high content of isotactic or syndiotactic sequences [13], P4VP shows exclusively an atactic structure [14] with an isotactic triad content varying only very slightly with the polymerization temperature. The lowest content (0.22) was obtained at 60°C in toluene using AIBN, and the highest (0.29) at − 78°C with PhMgBr or *n*-BuLi [12]. The polysalts prepared by the spontaneous process show higher isotacticity; demonstrating a propagation mechanism with a preferential isotactic placement.

In order to confirm the exceptional isotactic character of the 4-vinylpyridinium polymerization, the IR spectra of the polymers were determined. Fig. 2 shows the region relating to the backbone vibrations (1100–1040 cm^{-1}) for poly(4-vinyl-N-benzylpyridinium bromide)(P11) obtained at −30°C compared with that of P4VP prepared by radical polymerization at 60°C. The difference in the spectra may be interpreted by comparison with the results of Reynolds et al. [15] on polystyrenes (PS) of different tacticity. These authors demonstrated that the absorption bonds in the range 1100–1040 cm^{-1} depend strongly on the stereoregularity of the polymer. Atactic PS gives one broad band (maximum at 1069 cm^{-1}) while syndiotactic PS gives one strong band at 1030 cm^{-1}; however, for isotactic PS there are two bands of medium intensity at 1052 and 1083 cm^{-1} respectively. The two bands at 1053 and 1080 cm^{-1} in Fig. 2 are therefore consistent with an isotactic bias as concluded from the ^{1}H NMR spectra.

In Fig. 3, the isotactic triad content of polysalts is plotted as a function of polymerization temperature and compared to that of P4VP. A decrease of polymerization temperature favours the isotactic placement. This behaviour is indicative of a coordination polymerization process. In contrast, in radical polymerization and in ionic polymerization in solvents with high solvating power, syndiotactic placement is increasingly favoured as the polymerization temperature is lowered. Specific interactions, promoted by the quaternised structures, are therefore considered responsible for the

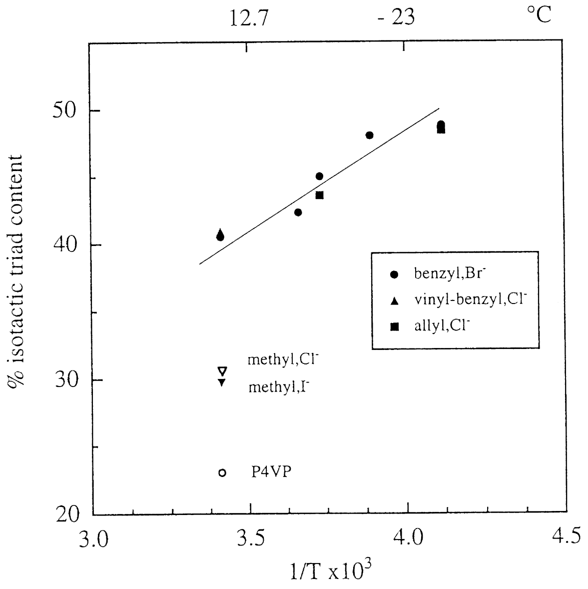

Fig. 3. Isotactic triad content of the polysalts vs. polymerization temperature.

tendency toward isotactic placement observed in the present work. Comparison of the isotactic triad content of the quaternized polymers obtained with the three different anions studied (Cl^-, Br^- and I^-) shows that the nature and size of the halogen counter ion have no influence. However, comparison of the results obtained for polysalts with different side chains demonstrates that here there is some effect. The isotactic triad content increases from about 0.30–0.40 when methyl group is replaced by benzyl, vinyl benzyl and possibly allyl groups. Usually steric and electrostatic repulsions between the substituents in the polymer chain favor the syndiotactic placement. This is not so in the present case and the size or the hydrophobicity of the alkylating agent are important parameters influencing the isotactic placement of the monomer. The results obtained at − 5°C and − 30°C respectively for benzyl bromide and 3-bromopropene (P9, P11 and P12, P13) and at 20°C for benzyl bromide and vinyl benzyl (P7 and P14), show similar isotactic triad content in spite of the difference of size of side chains. On this basis, it seems reasonable to attribute the effect of the nature of the alkylating agent to hydrophobic interactions between the side chains rather that to steric hindrance effect. Such type of interactions have already been proposed by Duran and Gramain [16] to interpret the isotactic placement observed with liquid crystalline polymethacrylates bearing biphenyl and spacer pendant groups.

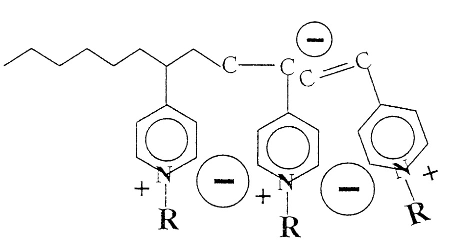

Fig. 4. Simulation of the addition of 4-vinyl-N-benzylpyridinium bromide to a growing chain of polysalts.

In order to interpret these observations, it is useful to recall the proposed mechanism for the spontaneous polymerization of quaternized 4-vinylpyridine. This polymerization can be considered as an anionic type polymerization promoted by the electronic delocalization of the pyridinium ion and involving the addition of a quaternized monomer to a macro-zwitterion. The mechanism may be compared to the classical anionic polymerization mechanism in non-polar solvents. In anionic polymerization in non-polar solvents, the stereoregularity of the polymers involves specific interactions between the counterion of the initiator, the last monomer units of the macromolecular chain and the monomer to be added [17]. In this mechanism, the nature and the size of the counteranion are important parameters. In spontaneous polymerization, there is no coordinated initiator, but it seems obvious that the propagating species is coordinated with the adding monomer. It is clear that the coordination is provided by the Coulombic interactions between the pyridinium group of the macro-zwitterion and the counter ion of the adding monomer as depicted in Fig. 4.

The observation that the nature and size of the halogen counter ion have no noticeable influence on the monomer placement may be understood as the sandwiched counter ion is well apart from the carbanion. Fig. 4 was examined from simulation by computer molecular modeling for 4-vinylpyridinium bromide. Computer optimization shows effectively that the energetically optimum placement of the adding monomer is determined by two types of interactions, the interaction between the double bond of the adding monomer and the carbanion of the propagating chain and the interaction between the two quaternary nitrogens with the anion sandwiched between them. As a consequence of the presence of the anion, the adding monomer is slightly tilted. It is worthwhile to remark that the sandwich placement is in agreement with the structural organization of mesogenic poly(4-vinylpyridinium)s proposed by Navarro-Rodriguez et al.[8]. These polysalts form smectic mesophases with single-layer head-to-tail arrangement of the mesogen-pyridinium side chains. In this organization, the anions are arranged in rows with the pyridinium rings sandwiched between them.

Fig. 4 allows one to explain the preferential isotactic placement and the influence of the analyzed parameters. Quaternization generates Coulombic interactions which increase with decreasing temperature notably as a consequence of the decreasing thermal agitation. Also, it is well understood that hydrophobic or Van der Waals interactions between the side chains are able to stabilize the sandwich formation.

4. Conclusion

Although the spontaneous polymerization of N-aryl or

N-alkyl 4-vinylpyridinium salts in solvents of high dielectric constant allowing a rapid quaternization of 4VP has been extensively studied, the tacticity of the obtained polysalts was never examined. We demonstrate that this particular anionic process leads to a preferential isotactic structure promoted by the attractive electrostatic interactions between the monomer and the growing chain and by hydrophobic or Van der Waals interactions between the alkyl or aryl side chains. The isotacticity increases with decreasing temperature as expected for Coulombic interactions. The preferred isotactic placement may be explained by the formation of a sandwich type complex between the quaternized monomer and the growing chain.

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