

Phase-Transfer in Synthesis of Ylidic Polymers by Polycondensation Processes

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Received: 3 December 1995; accepted 19 May 1996

ABSTRACT

The paper presents the synthesis and characterization of an ylidic polymer derived from monosubstituted carbanion of the dipyridylum ylide and 3,3-bis-(iodomethyl)oxetane, obtained by interphase-transfer polycondensation reaction. The synthesized polymers are characterized by elemental analysis and ^1H NMR, ^{13}C NMR and IR spectroscopy. The polymers obtained have low molecular weights, probably due to steric hindrances, chains polarity and interphase-transfer process.

Key Words: ylidic polymers, oxetane, dipyridyl, phase-transfer, characterization

INTRODUCTION

Phase-transfer catalysis (PTC) has been frequently used in the synthesis of polymers, due to its simplicity, low working temperature and linearity of the resulting polymers.

In our previous works, the synthesis of some polyethers and polyesters by PTC was presented [1-5]. Such polymers are obtained by polycondensation reaction between 3,3-bis-(chloromethyl)oxetane and various bisphenols or diacids, respectively, and some of them evidence, however, liquid crystalline behaviour [3, 5]. The presence of oxetanic rings in the main chain can induce special behav-

our, as due to its geometry. For example, in the case of polyesters, the presence of oxetanic rings explains the difficulties met in ordering of the polymer chains on cooling [3, 4]. As a consequence, the liquid crystalline properties appear only at first heating.

The most significant difficulty met in the synthesis of the polymers by PTC technique is that the polymers leave the organic phase during the reaction, and as a result low molecular weights are obtained. The molecular weights have been directly connected with the chains polarity; the most polar chains have generated the minimum molecular weight values ($M_n=3000$) [6].

Recently, synthesis of viologen polymers have been reported [7–9]. These types of polymers exhibit interesting optical and liquid crystalline properties [7, 8 and 10].

In this paper we report the synthesis and characterization of an ylidic polymer, derived from 4,4'-dipyridyl and 3,3-bis-(iodomethyl)oxetane.

EXPERIMENTAL

Instruments

The IR spectra have been recorded with a Perkin-Elmer 1310 spectrometer. The ^1H NMR and ^{13}C NMR spectra have been performed using a Bruker AM-400 spectrometer of 400.13 MHz and 100.62 MHz, respectively, in dimethyl sulphoxide ($\text{DMSO}-d_6$) and solid state.

Synthesis

N-Phenaclypyridinium bromide(III) has been synthesized by the salt method [11].

3,3-Bis-(iodomethyl)oxetane

3,3-Bis-(iodomethyl)oxetane(BIMO) has been obtained from 3,3-bis-(chloromethyl)oxetane (BCMO) [12] as follows: in a round-bottom flask a solution of NaI (0.3 mol) in acetone was prepared. Then BCMO (0.1 mol) was added and heated at 50°C on a water bath for 48 h. The NaCl formed was filtered and the organic solvent was distilled on a rotary evaporator. The crude crystals were pure enough for most practical purposes; mp= 49°C , and yield=99%.

Elemental analysis of BIMO (V) with molecular weight=338:

$\text{C}_5\text{H}_8\text{I}_2\text{O}$	%C	%H
Calculated	17.75	2.36
Found	17.70	2.40

IR Spectra, $\text{KBr}(\text{cm}^{-1})$: 3000, 2942, 2924, 2862, 1424, 1199, 1175, 980, 947, 801, etc.

^1H NMR Spectra, $\text{DMSO}-d_6$, $\delta(\text{ppm})$: 3.68, s, 4H,

$-\text{CH}_2\text{I}$; 4.24, s, 4H, $-\text{CH}_2\text{O}$.

Bis-ylide (VI)

Salt III (0.02 mol) was suspended in 200 mL dichloromethane in a separatory funnel. BIMO (0.01 mol) was dissolved in 50 mL dichloromethane and was added into the salt suspension. A solution of K_2CO_3 (0.06 mol) in 50 mL water was prepared. The latter solution was gradually added to the first mixture for 20 min with constantly shaking. The solution mixture was allowed to stand until the complete separation of the two layers took place. The organic layer was separated and dried over magnesium sulphate. The product was filtered and the solvent was removed on a rotary evaporator. The obtained solid product was purified by column chromatography (silica gel/dichloromethane and methanol); mp= 195°C (dec), yield=77%.

Elemental analysis of bis-ylide VI with molecular weight=476.57:

$\text{C}_{31}\text{H}_{28}\text{N}_2\text{O}_3$	%C	%H	%N
Calculated	78.13	5.92	5.88
Found	78.20	5.80	6.09

IR Spectra, $\text{KBr}(\text{cm}^{-1})$: 3047, 2951, 2869, 1712, 1692, 1636, 1592, 1576, 1359, 1269, 1196, 1070, 990 etc.

^1H NMR Spectra, $\text{DMSO}-d_6$, $\delta(\text{ppm})$: 3.84, s, 4H, CH_2/C^- ; 4.07, s, 4H, CH_2/O ; 7.20, 7.85, m, 10H, aromatic; 8.05, m, 2H, para/ N^+ ; 8.55, m, 4H, meta/ N^+ ; 9.05, m, 4H, ortho/ N^+ .

N-Phenacly-4,4'-dipyridylum Bromide (VIII)

4,4'-Dipyridyl (VII) (1.56g, 0.01 mol) was dissolved in 40 mL anhydrous acetone and was added to *o*-bromoacetophenone (1.99g, 0.01 mol) which had been dissolved in 40 mL anhydrous acetone. The mixture was allowed to stand for 48 h at room temperature.

The crude product was filtered, and the crystals obtained were pure, but were recrystallized from acetone; mp= 149°C , yield=87%.

Elemental analysis of product VIII, with molecular weight=355:

$C_{18}H_{17}N_2OBr$	%C	%H	%N
Calculated	60.84	4.22	7.88
Found	60.20	4.28	7.97

IR Spectra, $KBr(cm^{-1})$: 3456, 3034, 1695, 1621, 1445, 1235, 995, 779, 746, etc.

1H NMR Spectra, $DMSO-d_6$, $\delta(ppm)$: 6.62, s, 2H, CH_2 ; 7.76, t, $J=7.48$ Hz, 2H, meta/CO; 7.79, t, $J=7.48$ Hz, 1H, para/CO; 8.09, m, 4H, ortho/CO and meta/N; 8.77, d, $J=6.98$ Hz, 2H, meta/ N^+ .

^{13}C NMR Spectra, $DMSO-d_6$, $\delta(ppm)$: CH_2 , 65.89; CH, 123.03, meta/N; 125.20, ortho/N; 128.31, meta/CO; 129.19, ortho/CO; 134.78, para/CO; 146.78, meta/ N^+ ; 151.03, ortho/ N^+ ; C, 133.52, C bonded to CO; 140.87, para/N; 152.97, para/ N^+ ; 190.69, C in CO.

N,N-Bisphenacyl-4,4'-dipyridylum Dibromide (IX)

Salt VIII (3.55g, 0.01 mol) was placed in a 500 mL round-bottom flask, and dissolved in a mixture of 50 mL anhydrous acetone and 50 mL absolute ethanol. *o*-Bromoacetophenone (1.99g, 0.01 mol) was dissolved in 25 mL acetone, and added to the above mixture. The mixture was refluxed on a water bath for 4 h with magnetic stirring. After 2 h of reflux, a white crystalline compound began to separate. Finally the crystals were filtered and washed with anhydrous acetone, and obtained as pure product; mp=301 °C, yield=88%.

Elemental analysis of product IX, with molecular weight=554:

$C_{26}H_{22}Br_2N_2O_2$	%C	%H	%N
Calculated	56.31	3.97	5.05
Found	56.12	3.88	5.30

IR Spectra, $KBr(cm^{-1})$: 3027, 2945, 1691, 1639,

1593, 1450, 1332, 1229, 816, 782, 760 etc.

1H NMR Spectra, $DMSO-d_6$, $\delta(ppm)$: 6.65, s, 4H, CH_2 ; 7.68, t, 4H, $J=7.5$ Hz, meta/CO; 7.82, t, 2H, $J=7.5$ Hz, para/CO; 8.05, d, 4H, $J=7.5$ Hz, ortho/CO; 8.94 d, 4H, $J=7.0$ Hz, Meta/ N^+ ; 9.34, d, 4H, $J=7.0$ Hz, ortho/ N^+ .

^{13}C NMR Spectra, $DMSO-d_6$, $\delta(ppm)$: CH_2 , 66.37; CH, 128.33, meta/CO; 129.25, ortho/CO; 134.90, para/CO; 147.25, meta/ N^+ ; 149.46, ortho/ N^+ ; C, 133.46, C bonded to CO; 151.51, para/ N^+ ; 190.41, C in CO.

Bis-ylidic Polymer (XI)

Salt IX (5.54 g, 0.01 mol) was dissolved in 200 mL water in a separatory funnel and a solution of BIMO (3.38 g, 0.01 mol) in 150 mL nitrobenzene and a solution of 6.5 g K_2CO_3 in 50 mL water was prepared. The potassium carbonate solution, in 5 mL portions, was added to the first solution with vigorous shaking. After the addition of the last portion, the shaking was continued for further 20 min. The organic layer was filtered after the separation of the layers. The organic layer was diluted with methanol, and the polymer was separated as an intense blue violet solid product.

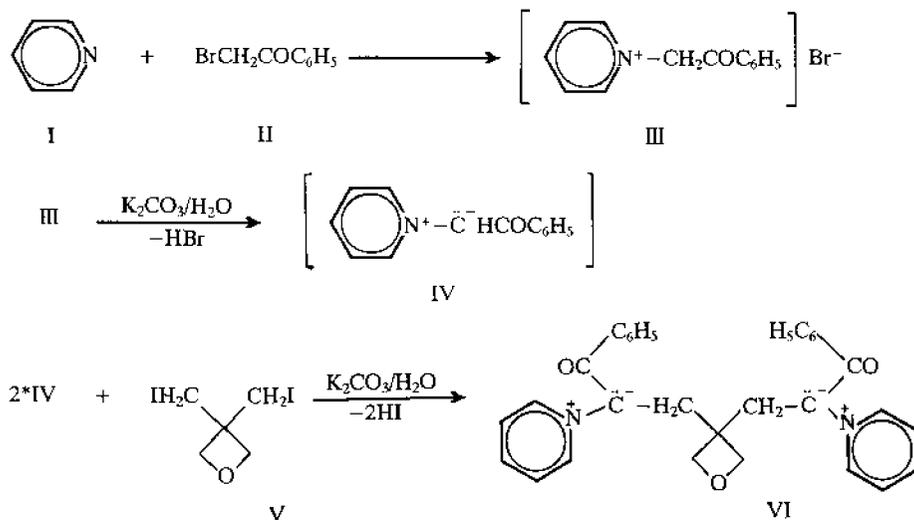
IR Spectra, $KBr(cm^{-1})$: 3020, 1680, 1640, 1595, 1545, 1490, 1410, 1320, 1195, 1090, 910, 895, 810, 695 etc.

^{13}C NMR Solid state: 62.82, CH_2/C^- ; 74.51, CH_2/O ; 128.97, 147.29, aromatic; 184.29, 189.82, CO etc.

RESULTS AND DISCUSSION

The basic nitrogen heterocycles react with ring substituted phenacyl bromides to produce *N*-phenacyl cycloimmonium bromides [13, 14]. These salts react with potassium carbonate to form the corresponding cycloimmonium ylides as stable compounds [15]. Often, in order to avoid their decomposition, these ylides are generated in situ as intermediate products.

Firstly, for verifying the possibility of reaction between a monosubstituted ylidic carbanion and BIMO we realized the synthesis of the bis-



Scheme I. The synthesis of the bis-ylide.

ylide VI (Scheme I).

Taking into account this result, we developed this kind of synthesis in order to obtain ylidic polymers by polycondensation between a monosubstituted ylidic carbanion and BIMO (Scheme II).

The pyridinium ylide (IV) generated in situ from *o*-bromoacetophenone (II), reacts with BIMO in the presence of potassium carbonate to form the bis-ylide VI. The attempts to obtain the bis-salt IX directly from 4,4'-dipyridyl VII and phenacyl bromide (*o*-bromoacetophenone) II failed, and only the mono-salt VIII was obtained. The bis-salt IX was obtained by treating the mono-salt VIII with phenacyl bromide. The bis-salt IX was dissolved in water and was treated with potassium carbonate to form the bis-ylide X. The bis-ylidic polymer was obtained by the aqueous polycondensation process using the aqueous solution of bis-ylide X and nitrobenzenic solution of BIMO.

The bis-ylide X may be separated and analyzed as a stable compound, but its ^1H NMR spectra show a mono-ylidic-mono-salt structure due to its sensitivity to pH.

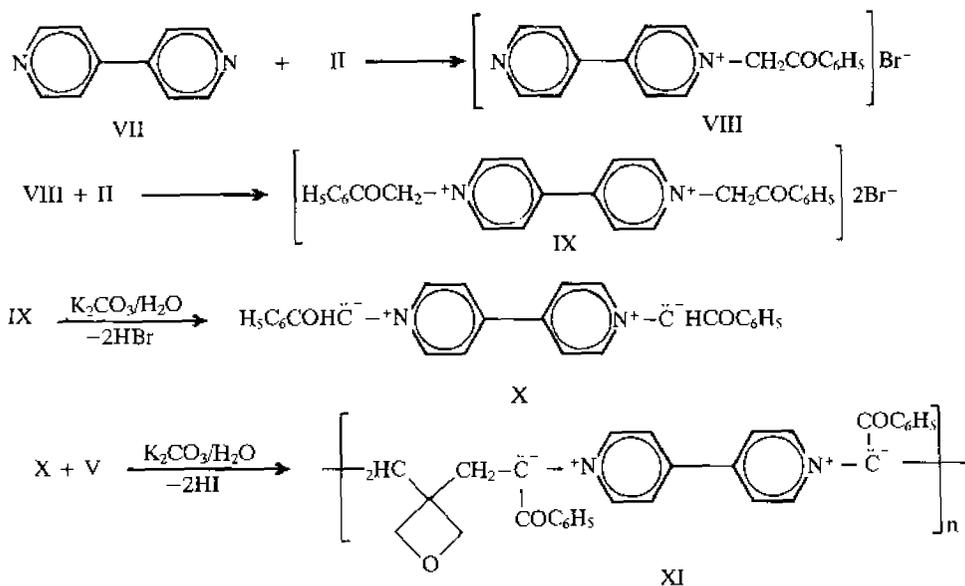
The structures of the compounds V, VI,

VIII, IX, and XI, reported for the first time in this paper, have been established by elemental analysis, IR, ^1H NMR and ^{13}C NMR spectra (in solution or solid state).

Unfortunately, we have obtained only low molecular weight polymers ($\bar{M}_n \approx 1900$; $\text{DP}=4$). Due to the method applied, the synthesis occurred in an excess of BIMO and, as a consequence, the resulting chains possess $-\text{CH}_2\text{I}$ end-groups ($\delta=4.24$ ppm). The molecular weights were determined as a ratio between the signals of $-\text{CH}_2\text{I}$ and pyridyl or oxetane groups of the ^1H NMR spectra (DMSO- d_6 as solvent).

The low molecular weights could be explained by taking into account the steric hindrances, chains polarity and interphase-transfer process. Thus, steric hindrance between oxetanic rings and $\text{C}_6\text{H}_5\text{CO}^-$ groups can reduce the reaction capacity.

In the second place, chains polarity can induce a high crystallization capacity with direct implications in polymers solubility. As a consequence, the polymer leaves the organic phase and the increase in chain length is stopped. This behaviour was previously reported for similar structures con-



Scheme II. The synthesis of the ylidic polymer

taining oxetanic rings [10]. Unfortunately, due to the intense blue violet colour of the organic phase, the crystallization process could not be observed.

The last reason for the low molecular weights could be the shifting of the equilibrium transfer of bis-ylide X from water to the organic phase on increasing the polymer concentration in the organic phase. Increase of the reaction time does not increase the molecular weight.

Supplementary studies are still necessary to elucidate the main factor responsible for the low molecular weights.

CONCLUSION

Ylidic polymers can be obtained by phase-transfer polycondensation from bis-dipyridylumphenacyl ylide and BMO. These ionic polymers can be easily obtained, but the molecular weights are very low; these results can be explained if considering steric hindrance, chains polarity and interphasic process.

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