A New Class of Conjugated Ionic Polyacetylenes. 3. Cyclopolymerization of Alkyldipropargyl(4-sulfobutyl)ammonium Betaines by Transition Metal Catalysts

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ABSTRACT: A new type of conjugated ionic polyacetylene was synthesized by metathesis polymerization of betaine monomers, alkyldipropargyl(4-sulfobutyl)ammonium betaines (ADPSAB). The alkyl groups used are ethyl, *n*-butyl, *n*-hexyl, and *n*-octyl. The polymerization of ADPSAB was carried out with various transition metal catalyst systems such as $MoCl_5$-, WCl_6-, and $PdCl_2$-based catalyst systems. The $MoCl_5$ and $PdCl_2$ were found to be particularly effective catalysts for the cyclopolymerization of the betaine monomers. ^{1}H-NMR, ^{13}C-NMR, IR, and UV−visible spectroscopies showed that poly(ADPSAB) possess polyene structure having cyclic recurring units in the polymer backbone. Unlike polyelectrolyte, the resulting polymers were more soluble and showed higher viscosities in the salt solution than in salt-free solution (antipolyelectrolytes). When doped with an acceptor such as iodine, the polymers exhibited a substantial increase ($\sim 10^{-3}$ S/cm) in electrical conductivity compared to the undoped state ($\sim 10^{-10}$ S/cm).

Introduction

There is considerable recent research and development in the field of conducting polymers such as doped polyaniline, polythiophene, and so on. Especially, polyacetylenes as simplest conducting polymers have been extensively studied by many researchers because of their unique properties such as conductivity, paramagnetism, and migration and transfer of energy.[1−4]

Recently, we have reported that W- and Mo-based catalyst systems are very effective for the cyclopolymerization of dipropargyl derivatives (nonconjugated terminal diynes), giving conjugated double bonds in the polymer backbone and a cyclic recurring unit.[5−15] The corresponding polymers have good solubility in common organic solvents, long-term stability toward oxidation, and high electrical conductivity. In the cyclopolymerization of the nonconjugated diynes as well as the polymerization of substituted acetylenes by transition-metal catalysts, the polymerization of ionic nonconjugated diynes has not been investigated so far because of its poor solubility in common organic solvents and the deactivating effect of polar ionic species on the Lewis-acidic transition-metal halide catalysts.

In a recent series of reports,[16−21] Blumstein *et al.* reported the synthesis of a new class of mono- and disubstituted ionic polyacetylenes with extensive conjugated backbones. The polymerization was achieved via activation of the acetylene bond in ethynylpyridines by introduction of strong electron-withdrawing substituents in conjugation to it.

In the previous reports, we described the first synthesis of substituted ionic polyacetylenes by metathesis catalysts.[22,23] The monomers used were dihexyldipropargylammonium salts with bromide, tosylate, and tetraphenylborate counterions. These polymers are polyelectrolytes in which counterions are associated with the fixed ionic charges on the polymer backbone to maintain electroneutrality.

In this paper, we deal with the synthesis of a new class of ionic polyacetylenes, polybetaines, by metathesis catalysts. Polybetaines are polymeric zwitterions with positive and negative charges on the same pendent groups, differing from polyelectrolytes in their solution behavior. The zwitterionic nature of polybetaine polymers provides various features that are useful in environmental and industrial application, e.g., as water and brine viscosifiers, variable-charge ion-exchange membranes, and selective chelating agents. The monomers used are alkyldipropargyl(4-sulfobutyl)ammonium betaines. And the alkyl groups used are ethyl, *n*-butyl, *n*-hexyl, and *n*-octyl. The prepared polybetaines are a new type of antipolyelectrolyte with an extensively conjugated backbone. The spectroscopic and physical properties such as solubility, thermal properties, electrical properties, and X-ray diffraction studies of the resulting polymers will be discussed. Also, unusual solution behavior upon salt addition will be mentioned.

Experimental Section

Materials. Alkyl amines (ethyl, *n*-butyl, *n*-hexyl, and *n*-octyl) and 4-butanesultone were used without further purification. Propargyl bromide (Aldrich Chemicals, 80% solution of tolune) was dried over calcium hydride and fractionally distilled. Tungsten(VI), molybdenum(V), and palladium(II) chloride (Aldrich Chemicals, 99+%) were used without further purification. Tetrabutyl tin and ethyl aluminum dichloride (Aldrich Chemicals) were used as received. All solvents used were purified in the usual manners.

Instruments for Characterization. ^{1}H- and ^{13}C-NMR spectra were recorded using a Bruker AC-300 spectrometer, and chemical shifts were reported in ppm units with tetramethylsilane (TMS) as the internal standard. Infrared spectra were measured using a Bomem MB-100 Fourier transform spectrophotometer using KBr pellets. UV−visible absorption spectra were obtained in formamide with a Shimadzu UV−3100S spectrophotometer. Thermal analysis was carried out with a Dupont TGA 9900 thermogravimetric analyzer in a nitrogen atmosphere at 10 °C/min. X-ray diffraction pattern of unoriented samples were obtained with a Rigaku Geigerflex X-ray diffractometer equipped with a Wahrus flat-plate camera using Ni-filtered Cu Kα radiation at a scan speed of 4°/min. Dilute solution viscosity measurements were made in CH_3-

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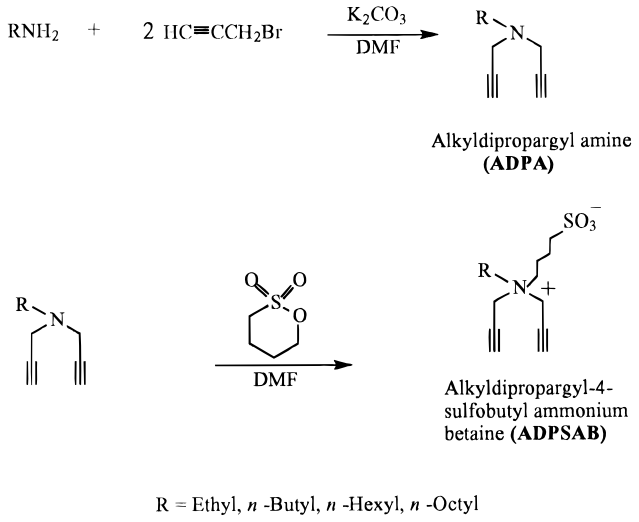
Scheme 1



R = Ethyl, *n* -Butyl, *n* -Hexyl, *n* -Octyl

OH-NaBr or aqueous solution at 30 °C using a Lauda viscometer. Electrical conductivity was measured by the four-point probe DC method. Elemental analysis was performed with a Perkin Elmer 240DS elemental analyzer.

Preparation of Film and Doping. The polymer films obtained from CF_3COOH solution were brittle and could not be used to measure the electrical conductivity. One approach to improve the physical properties of the polymers is to use them as blends with insulating polymers that possess good mechanical properties, thus combining the desirable properties of both polymers. We chose poly(vinyl alcohol) (PVA) as insulating polymer, because the hydrogen bonding between PVA and resulting polymers can greatly enhance the miscibility and homogeneity of the blends. Blending of these polymer was completed by vigorous stirring for 2 days in CF_3CO_2H solvent (weight ratio 50/50). The blended solutions of polymers were cast on a glass plate coated with dimethyldichlorosilane. The film was dried at room temperature for 2 days to evaporate most of the solvent slowly. The residual solvent was completely removed in vacuum. The homogeneity of the blends was investigated by the X-ray diffraction spectra. The iodine doping was performed by exposing the polymer films to iodine vapor in a vacuum desicator (initially at 10^{-1} mmHg) at 30 °C for 24 h. The dopant concentration was estimated by the weight uptake method.

Monomer Synthesis. Alkyl Dipropargyl(4-sulfobutyl)-ammonium Betaines (ADPSAB) (Scheme 1). A typical synthesis procedure is as follows: Alkylamine (0.1 mol) was added to 300 mL of DMF with K_2CO_3 (30.4 g, 0.22 mol). After 5 min, propargyl bromide (25 g, 0.21 mol) was slowly added to the stirred suspension, and the mixture was refluxed for 3 h. After the water was added, the solution was extracted with diethyl ether, and then the extract was dried over anhydrous $MgSO_4$. The solvent was evaporated by means of a rotatory evaporator and the alkyldipropargylamine (ADPA) was isolated by fractional distillation. To a DMF solution of ADPA (0.05 mol) was added 4-butanesultone (7.49 g, 0.055 mol) slowly dropwise, and the mixture was refluxed for 20 h. After the solvent was removed in a vacuum, the crude solid products, ADPSAB, were recrystallized from mixture of solvents.

Ethyldipropargyl(4-sulfobutyl)ammonium Betaine Monomer (EDPSAB). Ethyldipropargylamine (EDPA): yield 74%; bp 60−66 °C/10 mmHg; ^{1}H-NMR ($CDCl_3$) δ 1.0 (t, CH_3), 2.17 (t, ≡CH), 2.5 (q, CH_2 of CH_3CH_2-), 3.4 (d, CH_2C≡); ^{13}C-NMR ($CDCl_3$) δ 12.5 (C of CH_3), 41.5 (C of CH_2), 46.8 (CH_2 of CH_2C≡), 72.8 (C of HC≡), 78.5 (C of −C≡). EDPSAB was recrystallized from ethanol: yield 30%; mp 241−243 °C ^{1}H-NMR (D_2O) δ 1.4 (t, CH_3), 1.7−2.2 (m, internal $2CH_2$ of $(CH_2)_3SO_3^-$), 3.0 (t, ≡CH), 3.4−3.8 (m, $2CH_2$ of CH_2CH_3 and $CH_2SO_3^-$), 4.3 (s, $-CH_2C$≡); ^{13}C-NMR (D_2O) δ 9.9 (C of CH_3), 23.3, 23.9 (internal CH_2 of $(CH_2)_4SO_3^-$), 51.8, 52.7, 57.9 (carbons adjacent to N and SO_3^-), 60.8 (CH_2 of CH_2C≡), 73.0 (C of HC≡), 84.4 (C of −C≡). IR (KBr pellet) 3204, 2969, 2126 cm^{-1}. Elem Anal. Calcd for $C_{12}H_{19}NO_3S$: C, 56.01; H, 7.44; N, 5.44; O, 18.65. Found: C, 56.51; H, 7.48; N, 5.54; O, 18.55.

***n*-Butyldipropargyl(4-sulfobutyl)ammonium Betaine Monomer (BDPSAB).** Butyldipropargyl amine (BDPA): yield 64%; bp 86−88 °C/10 mmHg; ^{1}H-NMR (DMSO-d_6) δ 0.8 (t, CH_3), 1.3 (m, $-(CH_2)_3-$), 3.1 (t, HC≡), 3.3 (d, CH_2C≡); ^{13}C-NMR (DMSO-d_6) δ 13.7 (C of CH_3), 19.8, 28.7 (internal $-(CH_2)_2-$), 41.0 (C of N-CH_2-propyl) 51.1 (CH_2 of CH_2C≡), 75.3 (C of HC≡), 79.1 (C of −C≡); BDPSAB was recrystallized from methylene chloride and ethanol (4:1): yield 35%; mp 205−207 °C; ^{1}H-NMR (DMSO-d_6) δ 0.9 (t, CH_3), 1.3 (m, internal $2CH_2$ of $(CH_2)_3CH_3$), 1.6 (m, internal $2CH_2$ of $(CH_2)_3SO_3^-$), 3.3 (m, CH_2 adjacent to N or SO_3^-), 4.0 (s, ≡CH), 4.4 (s, CH_2C≡); ^{13}C-NMR (DMSO-d_6) δ 13.4 (C of CH_3), 19.1, 20.6, 22.2, 23.3 (internal CH_2 of $(CH_2)_3CH_3$ and $(CH_2)_4SO_3^-$), 49.4, 50.2 (CH_2 adjacent to N), 59.0, 59.2 (CH_2 of CH_2C≡ and $CH_2SO_3^-$), 71.6 (C of HC≡), 83.3 (C of −C≡); IR (KBr pellet) 3179, 2960, 2124 cm^{-1}. Elem Anal. Calcd for $C_{14}H_{23}NO_3S$: C, 58.92; H, 8.12; N, 4.91; O, 16.82. Found: C, 58.82; H, 8.23; N, 4.81; O, 16.92.

***n*-Hexyldipropargyl(4-sulfobutyl)ammonium Betaine Monomer (HDPSAB).** Hexyldipropargyl amine (HDPA: yield 68%; bp 72−82 °C/1 mmHg; ^{1}H-NMR (DMSO-d_6) δ 0.8 (t, CH_3), 1.2 (m, $(CH_2)_4$), 2.9 (t, HC≡), 3.3 (d, CH_2C≡); ^{13}C-NMR (DMSO-d_6) δ 13.0 (C of CH_3), 20, 21, 22, 25 (C of $-(CH_2)_4-$), 42, 51 (CH_2 adjacent to N), 73.3 (C of HC≡), 79 (C of −C≡). HDPSAB was recrystallized from n-propyl alcohol and acetonitrile (1:4): yield 35%; mp 141−143 °C; ^{1}H-NMR (DMSO-d_6) δ 0.9 (t, CH_3), δ 1.3, 1.6 (m, internal $6CH_2$ of $(CH_2)_5CH_3$ and $(CH_2)_4SO_3^-$), 3.3 (t, $3CH_2$ adjacent to N or SO_3^-), 4.1 (t, ≡CH), 4.4 (s, CH_2C≡); ^{13}C-NMR (DMSO-d_6) δ 13 (C of CH_3), 20, 21, 22, 22.2, 25, 30 (internal C of $(CH_2)_5CH_3$ and $(CH_2)_4SO_3^-$), 49, 50 (CH_2 adjacent to N), 59.0, 59.2 (CH_2 of CH_2C≡ and $CH_2SO_3^-$), 71.6 (C of HC≡), 83 (C of −C≡); IR (KBr pellet) 3290, 2943, 2123 cm^{-1}. Elem Anal. Calcd for $C_{16}H_{27}NO_3S$: C, 61.31; H, 8.68; N, 4.67; O, 15.31. Found: C, 61.41; H, 8.72; N, 4.58; O, 15.41.

***n*-Octyldipropargyl(4-sulfobutyl)ammonium Betaine Monomer (ODPSAB).** Octyldipropargyl amine (ODPA): yield 70%; bp 74−78 °C/0.1 mmHg; ^{1}H-NMR (CDCl3) δ 0.8 (t, CH_3), 1.2, 1.4 (m, $(CH_2)_5$), 2.1 (t, HC≡), 2.4 (t, CH_2 of CH_2N), 3.3 (d, CH_2C≡); ^{13}C-NMR ($CDCl_3$) δ 14.1 (C of CH_3), 22.6, 27.3, 27.4, 29.2, 29.4, 31.8 (C of $-(CH_2)_6-$), 42, 53 (CH_2 adjacent to N), 72.8 (C of HC≡), 78.8 (C of −C≡). ODPSAB was recrystallized from ethanol and ether: yield 40%; mp 164−166 °C; ^{1}H-NMR (DMSO-d_6) δ 0.8 (t, CH_3), 1.2, 1.6 (m, internal $8CH_2$ of $(CH_2)_7$-CH_3 and $(CH_2)_4SO_3^-$), 3.3 (t, $3CH_2$ adjacent to N or SO_3^-), 4.1 (t, ≡CH), 4.3 (s, CH_2C≡); ^{13}C-NMR (DMSO-d_6) δ 13.9 (C of CH_3), 20, 21, 22, 22, 25, 28, 28, 31 (internal C of $(CH_2)_7CH_3$ and $(CH_2)_4SO_3^-$), 49, 50 (CH_2 adjacent to N), 59.0, 59.5 (CH_2 of CH_2C≡ and $CH_2SO_3^-$), 71.6 (C of HC≡), 83 (C of −C≡) (see Figure 1); IR (KBr pellet) 3169, 2934, 2118 cm^{-1}. Elem Anal. Calcd for $C_{18}H_{31}NO_3S$: C, 63.31; H, 9.15; N, 4.10; O, 14.06. Found: C, 63.42; H, 9.17; N, 4.12; O, 14.04.

Polymerization. All procedures for catalyst system preparation and polymerization were carried out under a dry nitrogen atmosphere. Transition-metal halides and organometallic compounds were dissolved in the solvent mentioned in the polymerization table to make a 0.2 M solution before use. A typical polymerization procedure is as follows: Solvent, catalyst solution, and, when needed, cocatalyst solution were injected into a 20 mL ampule equipped with a rubber septum in the order given. When cocatalyst was used, the catalyst system was aged at 30 °C for 15 min. Finally, monomers dissolved in their respective solvents were injected into the polymerization ampule. After the mixture was allowed to react at 70 °C for 24 h, the polymerization was stopped by adding diethyl ether. The polymers were filtered off and washed with ethanol (to remove residual monomers). The resulting polymers were dried under vacuum at 30 °C for 24 h. The polymer yields were determined by gravimetry.

Results and Discussion

Polymerization of ADPSAB. Scheme 2 shows the polymerization of ADPSAB carried out with various transition-metal catalysts.

Table 1 lists the results of the polymerization of ODPSAB by using $MoCl_5$-, WCl_6-, and $PdCl_2$-based catalysts. The $MoCl_5$-based catalyst exhibited more effective catalytic activity than the WCl_6-based catalyst.

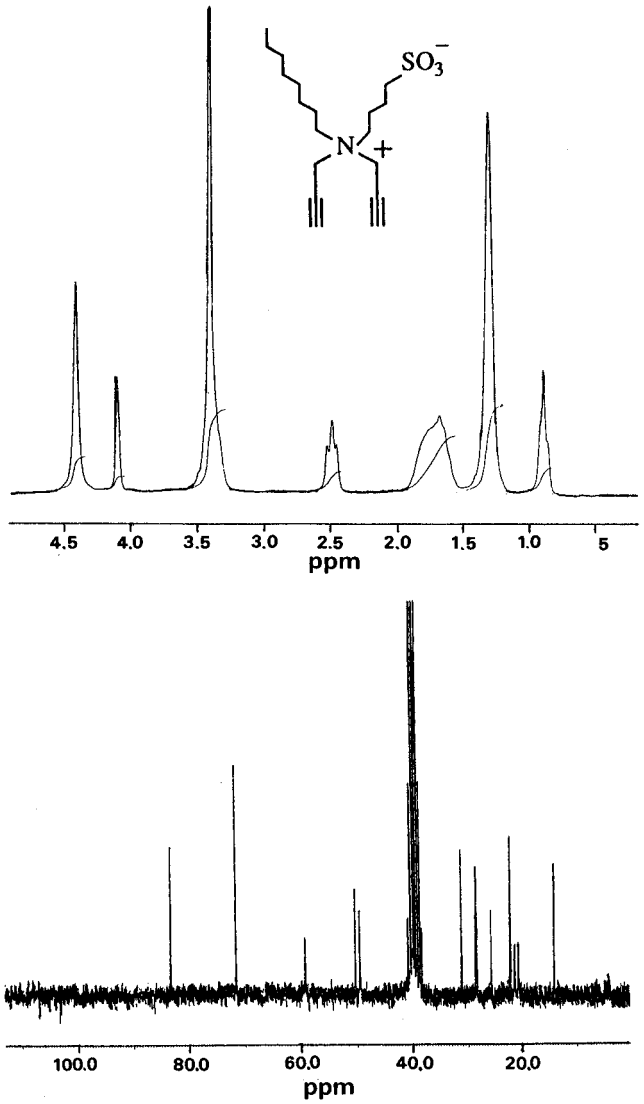
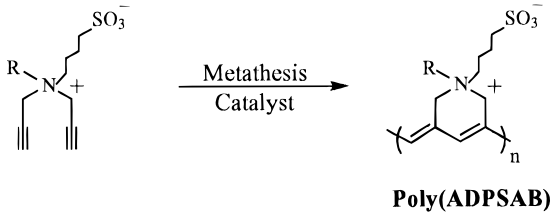


Figure 1. ^{1}H- and ^{13}C-NMR spectra of the ODPSAB in DMSO-d_6.

Scheme 2



Poly(ADPSAB)

R = CH_3CH_2 -, $CH_3(CH_2)_3$ -, $CH_3(CH_2)_5$ -, $CH_3(CH_2)_7$ -

Particularly, $MoCl_5$ alone polymerized ODPSAB effectively. Cocatalysts such as $EtAlCl_2$ and $(n\text{-}Bu)_4Sn$ exhibited a deactivating effect on the polymerization reaction. And, $PdCl_2$ showed most effective catalytic activity for the cyclopolymerizations of betaine monomers containing highly polar functional groups in polar aprotic solvents such as DMF and DMSO. The inherent viscosities (η_{inh}) and λ_{max} of poly(ODPSAB) are also listed in Table 1.

Table 2 lists the results of polymerizations of EDPSAB, BDPSAB, and HDPSAB by $MoCl_5$-, WCl_6-, and $PdCl_2$-based catalyst systems. In the case of both EDPSAB and BDPSAB, when Mo-based and W-based catalysts were used, we could not obtain any polymeric products. These results are probably due to poor solubility of the monomers with a short alkyl chain segment in the polymerization solvents such as chloroform, chlorobenzene, and dioxane. However, in the case of HDPSAB, with the long alkyl chain as compared to EDPSAB and BDPSAB, we could only obtain polymeric products in poor yield. And the results of the polymerization by $PdCl_2$ were similar to those obtained in the polymerization of ODPSAB. The polymeric products obtained were dark-red.

Table 1. Polymerization of the ODPSAB by Transition-Metal Catalysts[a]

expt no.	catalyst system (solvent)	polymer yield, %[b]	η_{inh}, dL/g[c]	λ_{max}, nm[e]
1	$MoCl_5$	78	0.18	470
2	$MoCl_5$ (CH_2Cl_2)	60	0.17	465
3	$MoCl_5$−$EtAl_2$ (1:4)	43	0.12	445
4	$MoCl_5$−$(n\text{-}Bu)_4Sn$ (1:4)	25		
5	WCl_6	33		
6	WCl_6−$EtAlCl^2$ (1:4)	25		
7	$PdCl_2$ (DMF)[d]	82	0.25	480
8	$PdCl_2$ (DMSO)[d]	90	0.30	405

[a] Polymerization was carried out in chloroform at 75 °C for 24 h. Initial concentration of monomer, $[M]_o = 0.2$. [b] Diethyl ether-insoluble polymer. [c] Inherent viscosity at 30 °C in methanol−NaBr solution. concentration, $C = 0.1$ g/dL. [d] Polymerized at 90 °C for 24 h. [e] λ_{max} in formamide.

Table 2. Polymerization of the ADPSAB by Transition-Metal Catalysts[a]

monomer	catalyst system (solvent)	polymer yield, %[b]	η_{inh}, dL/g[c]	λ_{max}, nm[e]
EDPSAB	$MoCl_5$ ($CHCl_3$)			
	$PdCl_2$ (DMF)	80	0.12	480
	$PdCl_2$ (DMSO)	60	0.086	450
BDPSAB	$MoCl_5$ ($CHCl_3$)			
	$PdCl_2$ (DMF)	80	0.11	480
	$PdCl_2$ (DMSO)	80	0.10	460
HDPSAB	$MoCl_5$ ($CHCl_3$)	20		400
	$PdCl_2$ (DMF)	85	0.05	380
	$PdCl_2$ (DMSO)	70	0.08	420

[a] Polymerization was carried out in chloroform at 75 °C for 24 h. $[M]_o = 0.2$. [b] Polymerized at 90 °C for 24 h. [c] Diethyl ether-insoluble polymer. [d] Inherent viscosity at 30 °C in aqueous solution. $C = 0.1$ g/dL. HDPSAB: In methanol/NaBr solution. [e] λ_{max} in formamide.

Polymer Structure. The polymer structure was identified by ^{1}H-NMR, ^{13}C-NMR, FT-IR, and UV−visible spectrophotometry. The ^{1}H-NMR and ^{13}C-NMR spectra of poly(ODPSAB) are shown in Figure 2. As the polymerization proceeded, acetylenic proton peaks of monomer at 4.0 ppm disappeared, the new peaks appeared at 6.0−8.0 ppm due to the protons on the conjugated double bond. In the ^{13}C-NMR spectrum, the olefinic carbon of poly(ODPSAB) broadly appeared at 120−140 ppm, while the acetylenic carbon peaks of the monomers at 71 and 82 ppm disappeared.

The IR spectrum of the polymer showed an absorption band at 1644 cm^{-1} due to the C=C stretch from the backbone carbons. Furthermore, the ≡CH and C≡C stretching band, at 3173 and 2118 cm^{-1}, respectively, that are present in the monomer, are absent in the polymer (see Figure 3). The hygroscopic nature of the polymer is evidenced by the broad and intense band at 3450 cm^{-1}.

The UV−visible spectra of poly(ODPSAB) were obtained in formamide (see Figure 4). A broad π−π^* absorption band due to the conjugated polyenes appeared at 300−650 nm. The absorption maxima of the polymers obtained by various catalyst systems increase in the following order: $PdCl_2$ ($\lambda_{max} = 480$) > $MoCl_5$ ($\lambda_{max} = 470$) > $MoCl_5$−$EtAlCl_2$ ($\lambda_{max} = 445$). Also, this order

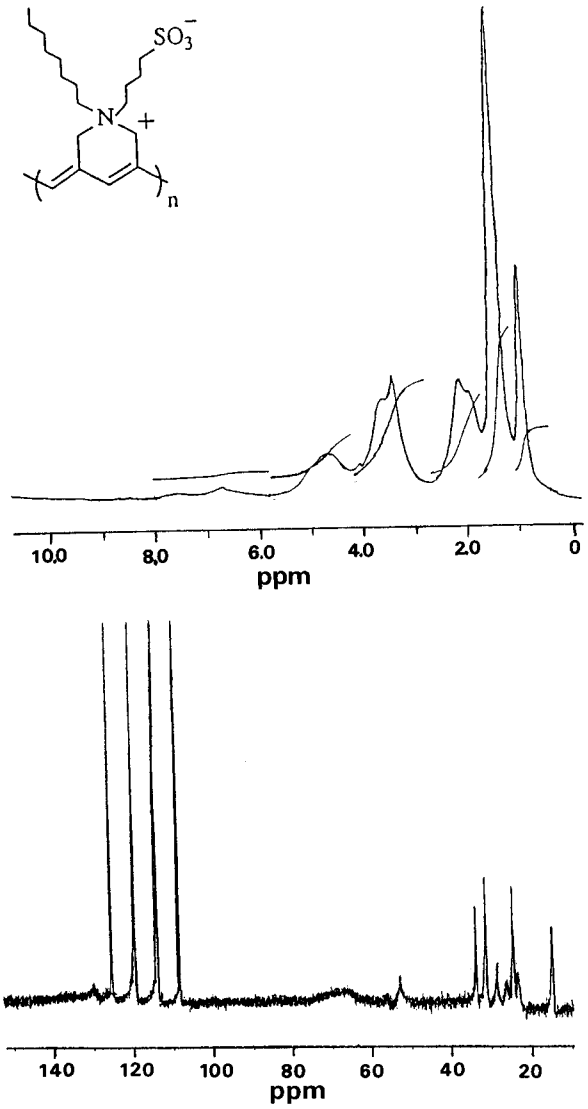


Figure 2. ^{1}H- and ^{13}C-NMR spectra of the poly(ODPSAB) in CF_3COOD. (Sample: expt no. 1 in Table 1).

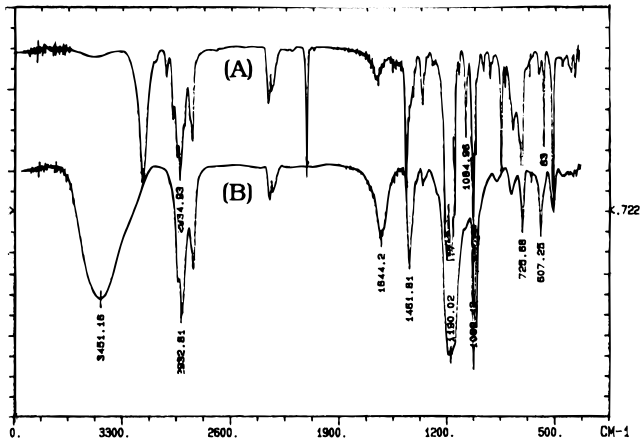


Figure 3. FT-IR spectra of the ODPSAB and poly(ODPSAB) in KBr: (A) ODPSAB, (B) poly(ODPSAB) (Sample: expt no. 1 in Table 1).

is in accord with trends of inherent viscosity. The ^{1}H- and ^{13}C-NMR spectra of poly(EDPSAB), poly(BDPSAB), and poly(HDPSAB) are similar to those of poly(ODPSAB). Figure 5 shows the UV−visible spectra of the resulting polymers prepared with $PdCl_2$ in DMSO solvent.

Polymer Properties. Table 3 shows the solubility behavior of resulting polymers. These zwitterionic

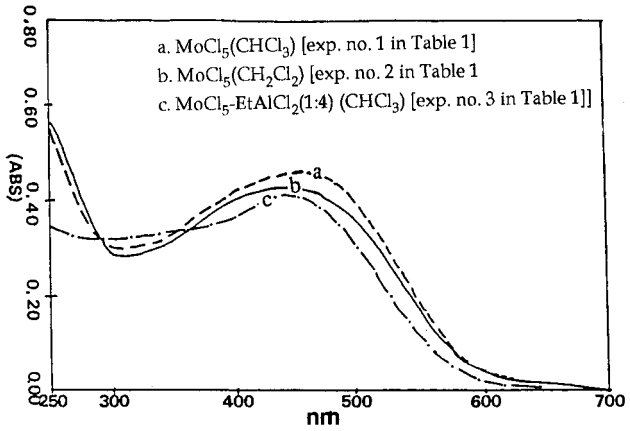


Figure 4. UV−visible spectra of the poly(ODPSAB) in formamide.

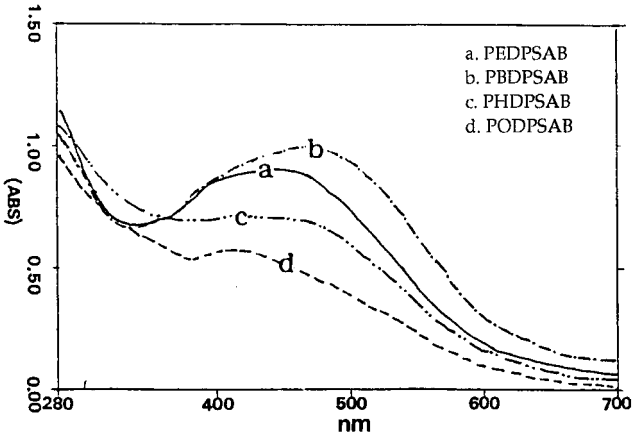


Figure 5. UV−visible spectra of the poly(ADPSAB) in formamide. The polymers were prepared with $PdCl_2$ in DMSO solvent.

Table 3. The Solubility Behavior of Poly(ADPSAB)[a]

	polymer			
solvent	PEDPSAB	PBDPSAB	PHDPSAB	PODPSAB
H_2O	+(+)	+(+)	−(+)	−(−)
MeOH	−(+−)	−(+)	−(+)	+−(+)
$HCONH_2$	+(+)	+(+)	+(+)	+(+)
HCO_2H	+(+)	+(+)	+(+)	+−(+)
CF_3CO_2H	+(+)	+(+)	+(+)	+(+)
ethylene glycol	+−(+)	−(+)	+(+)	−(+)
EtOH	−(−)	−(−)	−(−)	+−(+−)
DMSO	−(+)	−(+)	−(+)	+−(+)
DMF	−(−)	−(+−)	−(+−)	−(+−)
THF	−(−)	−(−)	−(−)	−(−)
toluene	−(−)	−(−)	−(−)	−(−)
n-hexane	−(−)	−(−)	−(−)	−(−)

[a] ( ): Salt-added solution. +: soluble. +−: partially soluble. −: insoluble.

polymers are soluble in polar protic solvents such as formamide, ethylene glycol, or organic acids capable of hydrogen bonding with the sulfonate anion. The polymer aggregated by the attractive intracharge-charge interaction could be considerably expanded by the strong hydrogen bonding between the pendant sulfonate anion and polar protic solvents. In particular, both poly(EDPSAB) and poly(BDPSAB) are soluble in water at room temperature, which is thought to be due to a short alkyl chain of pendant groups of polymers which did not restrict sterically and gave high ionic nature.

These poly(sulfobetaine)s are also soluble in organic polar protic solvent and more soluble in salt solution than in salt-free solution. Such an unusual solution behavior of poly(sulfobetaine)s is rationalized in terms

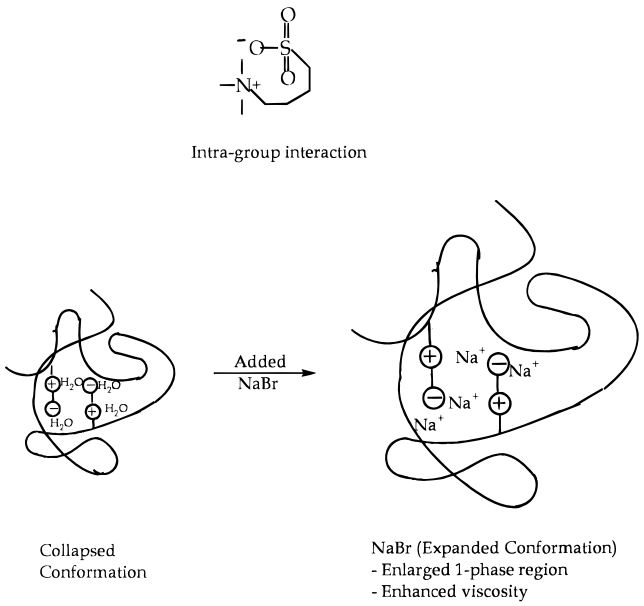


Figure 6. Proposed model of the poly(ADPSAB) in H_2O and NaBr.

of a shift from intra- to inter-interactions. Schulz, *et al.* proposed a schematic model to rationalize changes in the phase behavior and in the viscometric behavior of poly(sulfobetaine)s in H_2O and salt solutions.[24] Likewise, we propose a similar solution behavior of poly(ADPSAB) in H_2O and NaBr (see Figure 6). In H_2O, poly(sulfobetaine)s display extensive intra-associations. These associations are both of the intra-chain and intra-group type. The net effect is to vitiate the water-solubilizing effect of the ionic functionalities and render the polymer insoluble (or partially soluble). These strong intra-associations lead to phase separation. In contrast, the addition of a salt of intermediate solubilizing power like NaBr breaks up such intra-chain and intra-group associations and frees the zwitterionic functionality for aqueous solubilization of the polymer. Furthermore, the replacement of some H_2O molecules bound to the sulfonate anion with the positive ion (Na^+) may result in the increased net positive charge on the polymer backbone. The resulting repulsive force between the positive charges leads to the expanded chain conformation, which translates into an increased hydrodynamic diameter of the polymer and enhanced viscosity of the solution.

The poly(sulfobetaine)s are phenomenologically interesting by virtue of their "antipolyelectrolyte" solution behavior,[25,26] e.g. enhanced viscosities in salt solutions. Figure 7 is a plot of the inherent viscosity of poly(ODPSAB) in salt to that in methanol, for polymer in the semidilute solution region. Generally, the viscosity of a typical polyelectrolyte decreases with increasing salt concentration because polyelectrolyte is extended in water and is more collapsed in a salt solution. In contrast, the viscosity for the poly(sulfobetaine)s actually increases with increasing NaBr concentration, therefore, poly(ADPSAB) acts like an "antipolyelectrolyte".

The TGA curve for the polymers obtained showed weight loss starting at 170 °C and about 59% weight loss at temperature below 600 °C. Small weight losses exhibited at 140 °C are due to the evaporation of the hydration water in polymers, which is also suggested by the DSC experiments. The DSC thermograms for poly(ADPSAB) showed broad endothermic peaks at 140 °C, which are believed to be due to the evaporation of the hydration water.

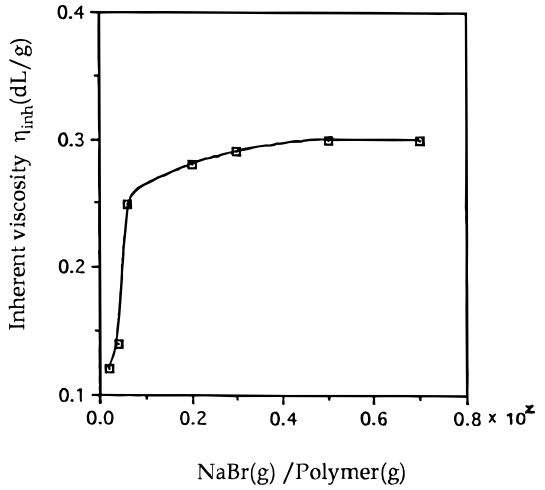


Figure 7. Inherent viscosity of the poly(ODPSAB) (Sample: expt no. 8 in Table 1), as a function of salt concentration. Inherent viscosity at 30 °C in methanol; $C = 0.1$ g/dL.

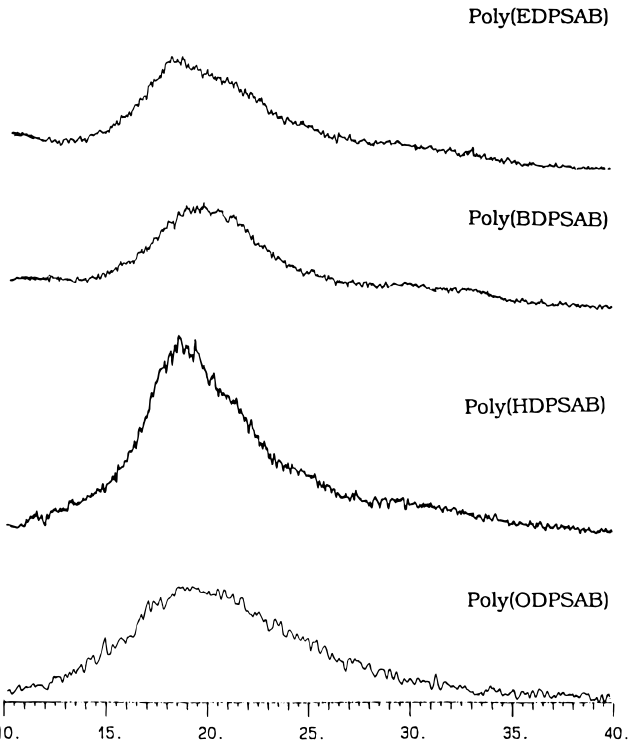


Figure 8. X-ray diffraction spectra of poly(ADPSAB) prepared with $PdCl_2$ (DMF).

X-ray diffractograms of the polymers obtained are shown in Figure 8. The range of the ratios of half-height width to diffraction angle ($\Delta 2\theta/2\theta$) for the present four polymers is 0.19−0.42. In general, the X-ray diffraction pattern of amorphous polymers is broad, and the values of $\Delta 2\theta/2\theta$ are greater than 0.35. On the other hand, crystalline diffraction peaks are sharp and their values of $\Delta 2\theta/2\theta$ are typically smaller than 0.05. In conclusion, the resulting polymers prepared are mainly amorphous.

The poly(ADPSAB) films cast from CF_3COOH solution were brittle and could not be used to measure the electrical conductivity. We prepared tough, free-standing films by blending these polymers with poly(vinyl alcohol) (PVA) in H_2O (or CF_3COOH).[27,28] The degree of homogeneity of the polymer blends with PVA was investigated by an X-ray diffraction experiment (see Figure 9). The high degree of crystallinity of PVA is known to arise from strong inter- and intramolecular hydrogen bonding. When poly(ADPSAB) chains intrude

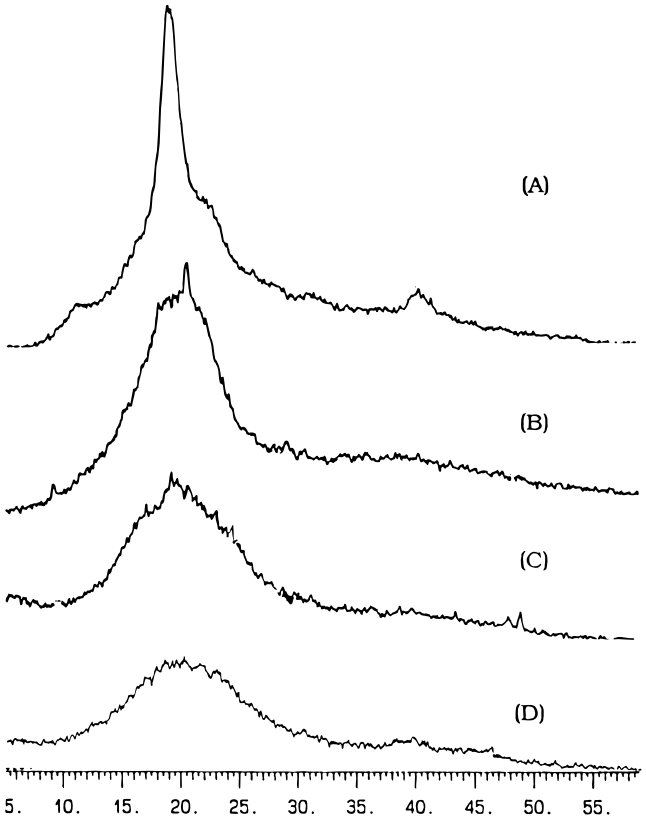


Figure 9. X-ray diffraction spectra of poly(BDPSAB) and its blends: (A) PVA, (B) 20% poly(BDPSAB) in the blend, (C) 50% poly(BDPSAB) in the blend, (D) poly(BDPSAB).

into the crystalline lattice, the hydrogen bonding between PVA chains is lost. X-ray diffraction spectra show no signs of crystallinity when the poly(ADPSAB) content in the blend reaches 20 wt %. The lack of evidence of new crystallite formation lends support to the assertion that polymer blending occurs at the molecular level. The blended polymer films exhibited low electrical conductivity in their undoped state ($<10^{-10}$ S/cm). When doped with an acceptor such as iodine, the poly(ADPSAB) showed a substantial increase in electrical conductivity, and highly doped polymer films exhibited conductivities of 0.8×10^{-3}–1.3×10^{-3} S/cm.

Conclusion

A new class of π-conjugated polybetaines were synthesized for the first time by cyclopolymerization of dipropargylammonium betaines with transition metal catalysts such as $MoCl_5$, WCl_6, and $PdCl_2$. $MoCl_5$ and $PdCl_2$ were found to be particularly effective catalysts. Unlike polyelectrolytes, the resulting betaine polymers were more soluble and showed higher viscosities in the salt solution than in the salt-free solution which is characteristic of antipolyelectrolytes. When doped with iodine, the polymers exhibited a substantial increase ($\sim 10^{-3}$ S/cm) in electrical conductivity compared to the undoped state ($<10^{-10}$ S/cm).

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