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Conjugated Ionic Polyacetylenes. 4. Polymerization of Ethynylpyridines with Bromine[1-5]

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ABSTRACT: A novel method for polymerization of the acetylenic bond in 2-ethynylpyridines is described. Formation of a donor–acceptor complex between the pyridine ring in the monomer and molecular bromine provides sufficient activation for the acetylenic triple bond to undergo spontaneous polymerization. The products obtained are substituted polyacetylenes with extensively conjugated backbones, wherein the side group pyridine rings are complexed to bromine in a 1:1 ratio. They are black or brown amorphous solids soluble in polar solvents, indicative of their ionic nature. Doping with acceptors such as iodine resulted in a substantial increase in their electrical conductivity compared to the undoped state.

Introduction

The utilization of electrically conducting polyacetylene in commercially viable applications is limited by its insolubility, poor mechanical properties, and lack of long-term stability, especially toward oxidation. Substituted polyacetylenes on the other hand, offer advantages of greater stability and better processability, but display substantially lower conductivities. This is largely due to structural and conformational restrictions arising from introduction of substituents which results in reduced conjugation. The design of synthetic methods for highly substituted polyacetylenes with extensively conjugated backbones possessing useful optical, electrical and magnetic properties is highly desirable, since they would retain important features such as processability and oxidative stability.

In a recent series of reports, we have described the synthesis of a new class of mono- and disubstituted ionic polyacetylenes with extensively conjugated backbones.[1-5] The disubstituted polyacetylenes obtained by us are unique with respect to their conjugated structures, which are hitherto unreported. These polymers are side-chain ionomers containing alkylpyridinium ring substituents that are associated with either halide or methanesulfonate counterions. Their synthesis is achieved via activation of the acetylenic bond in ethynylpyridines by introduction of a strongly electron withdrawing substituent in conjugation to it.[3,4] This results in spontaneous polymerization of the triple bond resulting in conjugated, ionic polyacetylenes.

These polymerizations involve the initial formation of alkylpyridinium salts via a Menschutkin reaction.[6,7] The acetylenic triple bond is activated by the strongly electron withdrawing pyridinium group conjugated to it, making it susceptible to nucleophilic addition by unquaternized monomer in the initiation step. Propagation involves a nucleophilic attack of the resulting carbanion on the triple bond of quaternized monomer molecules.[4] Since this step involves a highly reactive vinyl carbanion and activated monomer, its efficiency is dependent on the rate of generation of the quaternized species. Scheme I shows the proposed mechanism for the polymerization reaction. The Menschutkin reaction on 2-substituted pyridines is relatively slow;[8] it is, therefore, most likely to be the rate-determining step in these polymerization processes. Furthermore, the vinylic carbanion which adds to the triple bond of the quaternized monomer in the propagation step can also undergo alkylation by the quaternary species (Scheme I). This would result in more chain terminations, thus precluding the formation of high molecular weight polymers. In view of this limitation, alternative methods were sought to activate the acetylenic bond in ethynylpyridines.

The present report describes polymerization of the acetylenic bond in ethynylpyridines by the formation of a donor–acceptor complex between the pyridine nitrogen and molecular bromine. The reaction of 2-ethynylpyridine and its trimethylsilyl derivative with bromine resulted in the initial formation of a pyridine–bromine complex, which provides sufficient activation for the triple bond to undergo spontaneous polymerization.[9] The products, poly[(2-*N*-bromopyridiniumyl)acetylene bromide] complexes (VIp, VIIp), are black and brown solids, respectively, indicating conjugated backbones. Figure 1 shows the proposed structures for these polymers.

Experimental Section

Materials. 2-Ethynylpyridine and 2-[2-(trimethylsilyl)ethynyl]pyridine were obtained from Farchan Laboratories and

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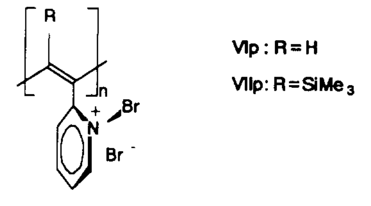
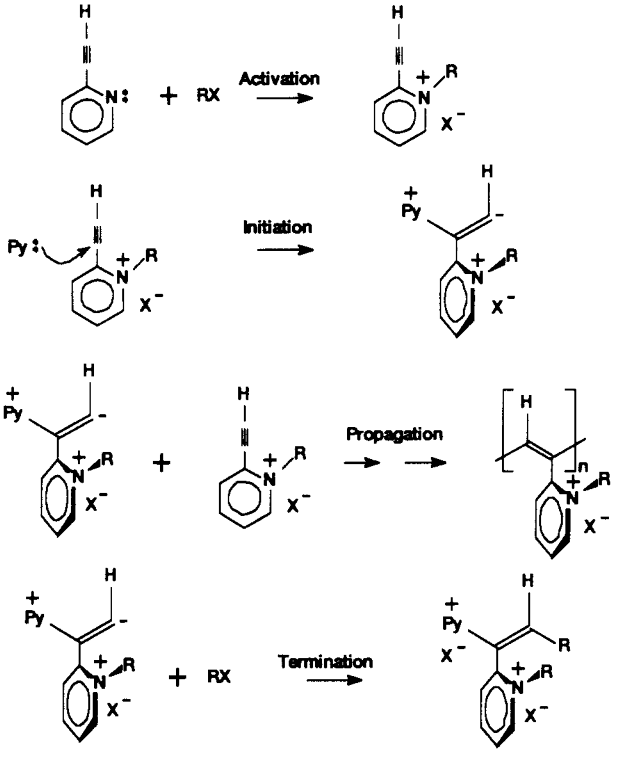


Figure 1

Scheme I
Proposed Mechanism for Polymerization of Ethynylpyridines via Quaternization



R = alkyl; X = Br⁻, I⁻, $CH_3SO_3^-$; Py : = unquaternized monomer

distilled under vacuum before use. Bromine was obtained from Aldrich Chemical Co. and was used without further purification. Commercially available iodine was purified by sublimation under reduced pressure for doping studies.

Measurements. Infrared spectra were recorded on a Perkin-Elmer 1600 Series Fourier transform spectrophotometer using KBr plates. UV absorption spectra were obtained at 22 °C in DMSO on an IBM 9420 visible–ultraviolet spectrophotometer. Thermal analyses were carried out on a DuPont TGA 2950 thermogravimetric analyzer. X-ray diffraction patterns of unoriented samples were obtained on a Rigaku Geigerflex X-ray diffractometer equipped with a Wahrus flat-plate camera using Ni-filtered Cu α radiation. Dilute solution viscosity measurements were made in DMSO at 28 °C using a Cannon Ubbelohde dilution-type viscometer. Fluorescence spectra were obtained on a Perkin-Elmer MPF-44B fluorescence spectrophotometer equipped with a PE 150 xenon source in conjunction with a Stanford Research System Model SR440 DC-300MHz amplifier and a SR400 two-channel gated photon counter. All spectra were recorded in DMSO at 22 °C. Conductivity measurements were carried out using a technique described previously.[3] Elemental analyses were done at Atlantic Microlabs, Atlanta, GA.

Poly[(2-*N*-bromopyridiniumyl)acetylene bromide] Complex (VIp). Bromine (0.8 g, 0.005 mol) was added dropwise to 2-ethynylpyridine (0.5 g, 0.005 mol) at room temperature or at 0 °C with stirring. An exothermic reaction ensued with the formation of a black solid. The product was washed several times with ether and dried under vacuum to yield the polymer as a black powder (1.2 g) readily soluble in alcohol and DMSO: IR (cm^{-1}) 3400 (ring =C—H stretching), 1617 (—C=C— stretching), 1018 (pyridine ring vibration mode in complex); UV, λ_{max} C=C (nm) 470; η_{inh} (dL/g) 0.1. Anal. Calcd: C, 32.10; H, 1.54; N, 5.34; Br, 61.02. Found: C, 33.91; H, 2.10; N, 5.57; Br, 58.16.

Poly[2-[2-(trimethylsilyl)ethynyl]-*N*-bromopyridiniumyl bromide] Complex (VIIp). 2-[2-(Trimethylsilyl)-ethynyl]pyridine (0.5 g, 0.003 mol) was reacted with bromine (0.45 g, 0.003 mol) in an identical manner. The reaction mixture turned brown with the precipitation of a brown-black solid. This was extracted several times with ether and dried under vacuum to yield the title polymer. It was readily soluble in DMSO, alcohol, and chloroform: IR (cm^{-1}) 3409 (ring =C–H stretching), 1607 (—C=C— stretching), 996 (pyridine ring vibration mode in complex); UV, λ_{max} C=C (nm) 450 (shoulder); η_{inh} (dL/g) 0.1.

Doping Procedure. Iodine doping was done by the vapor deposition method described previously.[4,10]

Results and Discussion

The polymer obtained from the bulk reaction between 2-ethynylpyridine and bromine is a lustrous black solid, indicative of a highly conjugated structure as shown in Figure 1. The infrared spectrum shows a broad, intense band at 3400 cm^{-1} that arises from the C=C—H stretching in the pyridinium rings that are strongly hydrogen bonded.[11] This band is characteristic of all polymers reported by us, including those obtained by the quaternization method,[1-4] and is indicative of their ionic nature. The possibility of backbone =C—H stretching being responsible for this band as reported by Deits et al. for poly(cyanoacetylene)[12] was ruled out, since both the disubstituted polyacetylene VIIp and those synthesized by the previously reported method exhibited this band.[4] The presence of hydrated water is also unlikely, since samples heated in vacuum for several hours showed no substantial change in the intensity of the band. A strong band at 1611 cm^{-1} for VIp and 1607 cm^{-1} for VIIp (—C=C— stretching) was observed, indicating extended conjugation in the polymer backbones. The ≡C—H and the —C≡C— stretching bands at 3290 and 2108 cm^{-1}, respectively, that are present in the monomers are absent in the product polymers. Figure 2 shows the IR spectra of the starting monomer and polymer VIp. Evaluation of the cis and trans content in the polyacetylene backbone from C=C stretching bands for the present systems is complicated by the fact that the fairly intense band around 1015–1019 cm^{-1} (trans C=C) could also arise from symmetric ring vibration of the side group pyridine rings upon complexation with bromine. The 740-cm^{-1} band (cis C=C) is, however, very weak, implying very small cis content. The UV–visible spectra of the product polymers provide additional evidence for the extended conjugation when compared with that of the monomer (Figure 3). The absorption maximum for the conjugated backbone (λ_{max}) in polymer VIp occurs at 470 nm trailing to ~800 nm. This backbone conjugation is similar to those observed for the poly[(2-*N*-alkylpyridiniumyl)acetylene bromides] obtained by quaternization of the monomer with alkyl halides.[1-4] The absorption spectrum for VIIp exhibited a shoulder at 450 nm indicating lower conjugation probably resulting from chain twisting caused by the sterically bulky trimethylsilyl substituent. Both polymers are readily soluble in polar organic solvents. X-ray diffractograms of an unoriented sample of VIp indicate amorphous scattering with a broad ring at 11.83 Å, possibly due to a layered structure.

The present polymerization reactions are exothermic, resulting in temperature increases of ~20 °C upon addition of bromine to the monomer at room temperature. A similar exothermicity was observed when the reaction was conducted at 0 °C. Both methods, however, gave product

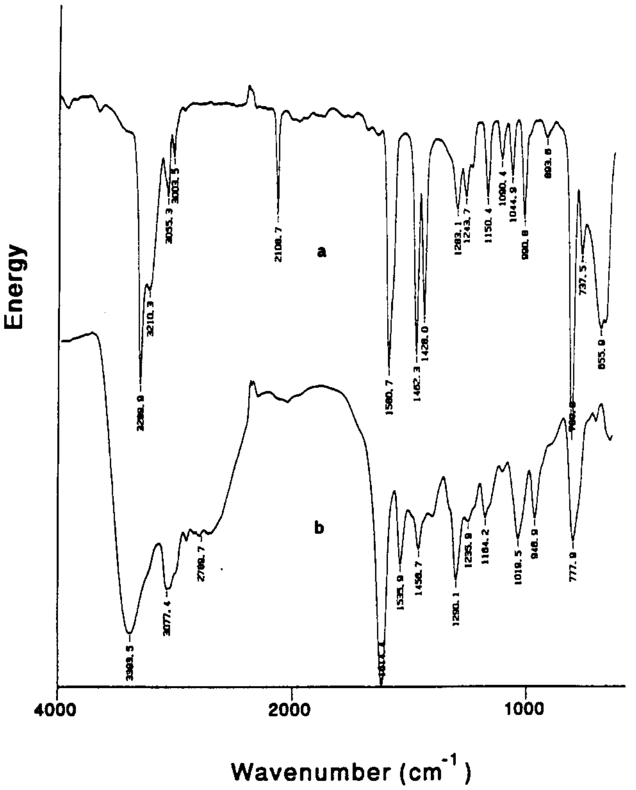


Figure 2. FTIR spectra of (a) 2-ethynylpyridine and (b) polymer VIp.

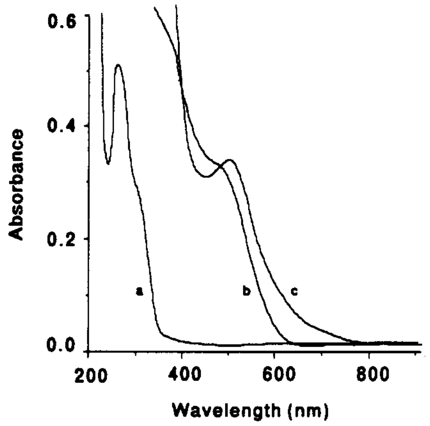


Figure 3. UV–visible spectra of (a) 2-ethynylpyridine, (b) VIIp, and (c) VIp.

polymers that are spectrally similar. The mechanism appears to be similar to that proposed for polymerization of ethynylpyridines[4] (Scheme I) and for vinylpyridines[13,14] via quaternization by alkyl halides. The low inherent viscosities for the present polymers are indicative of their low molecular masses, possibly due to rapid termination of the growing polymeric chains by bromine. The absolute values of M are, however, difficult to measure in view of the strongly colored and charged nature of these systems.

The formation of donor–acceptor complexes of pyridine with halogens and mixed halogens is well documented in the literature.[15,16] In the halogen group, the tendency increases with increasing polarizability of the inter-halogen bond. Thus the acceptor tendency increases from chlorine to iodine.[17] The structural characteristics of the complex depends on the nature of the halogen acceptor. Complexes involving I_2 or ICl have been found to be ionic due to the highly polarized inter-halogen bond, while those with Cl_2 or Br_2 were reported to be largely neutral due to their lower polarizability.[15] This is also reflected by the relatively greater stability of the former type. The low molecular pyridine complex with bromine, for example, is unstable and decomposes readily in air with elimination of bromine.[14] This is attributed to the resulting complex being of the neutral type, which involves a relatively weak dipolar interaction between pyridine and molecular bromine. In the present polymers, however, the pyridine–bromine "polycomplex" appears to be ionic in nature, which is reflected by its indefinite stability at ambient temperatures. The presence of the acetylenic substituent on the pyridine ring thus appears to favor the polarization of the inter-halogen bond in the present complexes, providing rare examples of enhanced stability in such systems. TGA thermograms of polymer VIp showed a rapid weight loss starting at 100 °C. This is attributed to loss of bromine by thermal elimination. A small decrease in sample weight was observed starting at 40 °C, which is reflected in the small deviations in their analytical data. The disubstituted polymer VIIp displayed relatively greater stability, with degradation beginning only at 150 °C. Both polymers are thus less stable than polymers obtained by the quaternization method, where no degradation was observed until 240 °C.

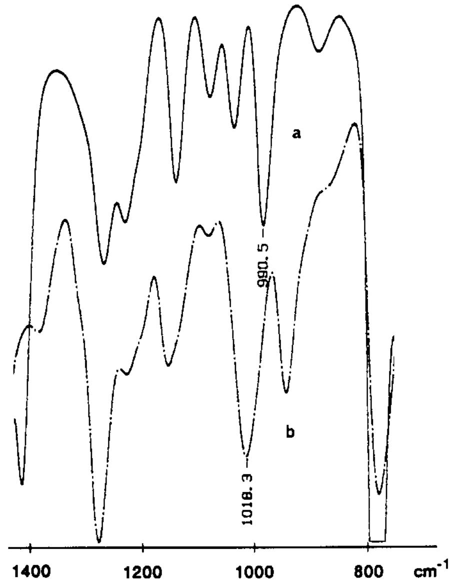


Figure 4. FTIR spectra of (a) uncomplexed 2-ethynylpyridine and (b) polymer VIp complexed with bromine.

The formation of pyridine–halogen n–σ complexes results in marked changes in the infrared spectra compared with that of uncomplexed pyridine. The most prominent change occurs in the symmetric ring vibration mode of the uncomplexed pyridine ring at 990 cm.$^{-1}$, which is shifted to higher frequencies (~1000 cm^{-1}).[14,18] The magnitude of this shift ranges between 10 and 15 cm^{-1}, depending on the type of acceptor and the substitution pattern in the pyridine ring. In polymer VIp, complex formation between the pyridine side groups and bromine is evidenced by a shift of the symmetric ring vibration band from 990.5 (uncomplexed monomer) to 1018 cm^{-1} (Figure 4). A similar shift from 989.5 to 996.4 cm^{-1} was observed for VIIp as a result of complex formation. This effect, which arises due to the electronegative atom being bonded to the pyridine nitrogen, is absent in the polymers obtained by the quaternization method wherein the pyridine nitrogen is bonded to a carbon atom of an alkyl chain.[3,4]

The emission spectrum of the polymer VIp showed a broad fluorescence band centered at 560 nm at room temperature, whose intensity is largely independent of dilution

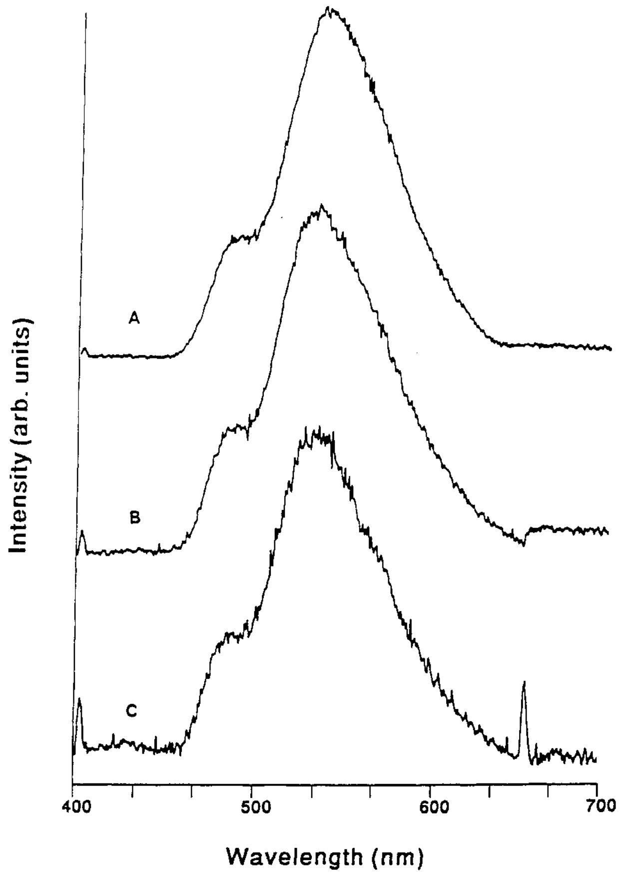


Figure 5. Fluorescence spectra of polymer VIp for different concentrations: (A) 2.6×10^{-3}, (B) 5.2×10^{-4}, and (C) 2.6×10^{-5} g/L.

(Figure 5). This phenomenon is indicative of intramolecular excimer formation involving the pendant pyridine rings. Similar excimer formation has been observed by us for the ionic polyacetylenes obtained via quaternization and has also been reported for protonated poly(vinylpyridines)[19] and isotactic polystyrene.[20,21] It is attributed to efficient stacking between neighboring aromatic side groups. Although measurements were not made at 77 K (instrument limitation), at which normal excimer emission is expected to disappear due to "freezing" of random conformations in polymers with saturated backbones thereby preventing energy transfer between side group chromophores, we believe that the present systems would not exhibit this behavior. This is in view of their conjugated unsaturated backbones, which predetermines the conformation of the side group pyridine chromophores. The configuration required for energy transfer is therefore built up in the polymer chains prior to excitation. Similar observations were made by Ishii et al.[19] for protonated poly(2-vinylpyridine), which exhibits a "dimerlike excimer" due to interaction between protonated pyridine rings adjacent to one another.

In the present polymers, such excimer formation is indicative of a highly conjugated backbone with minimal twist, which is a prerequisite for efficient stacking of the pyridine rings. In our systems, such stacking seems to be largely due to a strong electrostatic interaction of each counterion with two adjacent pyridinum rings. The fluorescence emission due to intramolecular excimer formation of polymer VIp was also confirmed by the fact that its emission spectrum at 560 nm is essentially the same as its absorbance spectrum. The monomer emission occurs at ~290 nm, which is in the same range as those for 2-ethylpyridine and 2-vinylpyridine.[19] Results obtained from modeling studies on these ionic systems using dynamic simulation methods[22] provide additional support for stacking of the aromatic substituents. In contrast to VIp, polymer VIIp did not exhibit strong fluorescence in its emission spectrum, since efficient side group stacking is precluded by a larger backbone twist due to steric factors imposed by the bulky trimethylsilyl substituent.

Table I
Electrical Conductivity of Polymer VIp

		conductivity, S cm^{-1}	
time, h	dopant uptake, wt %	undoped	doped
0.75	168	$<10^{-9}$	6.6×10^{-4}
1.00	173	$<10^{-9}$	7.0×10^{-4}
140	380	$<10^{-9}$	6.0×10^{-3}

The polymerization of 2-ethynylpyridines with bromine described here differs greatly from that of 4-vinylpyridine and bromine reported by Kuzyakov et al.[23] According to these authors, the latter reaction initially involves an electrophilic addition of bromine across the vinylic double bond, followed by polymerization via quaternization of the pyridine nitrogen by the resulting dibromide. The product polymer was reported to be a main-chain polyelectrolyte of the ionene type. A similar reaction is precluded in the present case due to the following reasons: (i) electrophilic addition of bromine across the acetylenic triple bond is extremely difficult and is hence unlikely; (ii) an ionene-like polymer would not undergo thermal elimination of bromine. Furthermore, it would result in a polymer that does not possess a polyacetylenic backbone, which is contrary to the observed similarities with the polymers obtained by the quaternization method. The long-wavelength emission observed in the fluorescence spectrum of the polymer VIp also suggests that the pyridine rings are present as side groups attached to a polyene backbone.

The present polymers exhibited poor electrical conductivity in their undoped state ($<10^{-9}$ S cm^{-1}). When doped with an acceptor such as iodine, polymer VIp showed a substantial increase in electrical conductivity. The polymer showed great affinity for iodine; large, irreversible iodine uptake (>350% by weight) were recorded. Highly doped polymer films exhibited conductivities of 10^{-3} S cm^{-1}. Table I lists the dopant with time and the conductivity of the iodine-doped polymer. This behavior was similar to the ionic polyacetylenes reported by us previously.[4,10,24] A charge-transfer complex of similar nature between poly(vinylpyridine) and iodine in a 1:10 ratio has been reported recently.[25] It was found to be ionic, with the side group pyridine rings interacting with polyiodide chains generated from the dopant. In the present polymers, the large, irreversible iodine uptake is also indicative of the ionic character of the complex, which results in strong interaction with the polyiodide (I_3^- and I_5^-) species generated from the dopant.

In summary, the spontaneous polymerization reaction of ethynylpyridines in the presence of bromine resulting in substituted polyacetylene–halogen donor–acceptor complexes offers a new and relatively simple route for the synthesis of highly conjugated, substituted polyacetylenes. The proposed structure involves an extensively conjugated backbone with side group pyridine rings complexed with bromine. The stability of this polycomplex to degradation at ambient temperature is in contrast to the poor stability of the monomeric complex between pyridine and bromine and provides rare examples of stable pyridine–halogen n–σ polycomplexes. This is largely due to their ionic nature, which differs from that of the monomeric type that is neutral. The strong absorption bands in the infrared spectra due to hydrogen-bonded ring =C—H stretch, long-wavelength excimer fluorescence in the emission spectrum, and the irreversibility of the uptake of iodine provide additional support for the ionic nature of the complex. The properties of the present polymers are similar to those of the ionic polyacetylenes reported by us that were obtained by the quaternization method. The substantial increase in the conductivity of the iodine-doped polymer VIp and its good solubility offer advantages of improved processability that may be suited for potential applications.

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Registry No. VIp (copolymer), 137536-24-4; VIIp (copolymer), 139242-74-3; I_2, 7553-56-2.