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Articles

Cyclopolymerization of *N*,*N*-Dipropargylamines and *N*,*N*-Dipropargyl Ammonium Salts

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ABSTRACT: The cyclopolymerization of polar, ionic *N*,*N*-dibutyl-*N*,*N*-dipropargylammonium bis(trifluoromethylsulfonyl)imide (**M1**), *N*,*N*-dimethyl-*N*,*N*-dipropargylammonium bis(trifluoromethylsulfonyl)imide (**M2**), *N*,*N*-dipropargylmorpholinium bis(trifluoromethylsulfonyl)imide (**M3**), and *N*-propyl-*N*,*N*-dipropargylamine (**M4**) using five different well-defined Schrock- and trifluoroacetate-modified Grubbs-type initiators was investigated. Ru-based initiators allowed for the polymerization of **M1**−**M3** with average isolated polymer yields around 25−40%, however, poly-**M2** and poly-**M3** thus prepared consisted >95% of five-membered ring structures, i.e., (3,4-(1*H*-2,5-dihydropyrrolylene)vinylene)s units. In contrast, the use of the Schrock type initiator Mo(N-2,6-$i\mathrm{Pr_2C_6H_3}$)($\mathrm{CHMe_2Ph}$)($\mathrm{OC(CH_3)(CF_3)_2}$)$_2$ allowed for quantitative polymer yields, whereas, poly-**M2** prepared by the action of this initiator was based on both five- and six-membered, i.e., (3,5-(1,2,5,6-tetrahydropyridinylene)-methylidene) cyclic units. Polymers were synthesized with molecular weights $M_n < 21\,800$ g/mol and polydispersity indices in the range of $1.04 < \mathrm{PDI} < 1.37$ and $1.01 < \mathrm{PDI} < 1.08$ with Ru- and Mo-based initiators, respectively. They were additionally investigated for their thermal stability and ionic conductivity. Finally, the solvatochromic behavior of the polymers prepared was studied. Particularly, solutions of poly-**M1** prepared by the action of Ru-based initiators displayed a high sensitivity toward traces of water in *N*,*N*-dimethylformamide.

Introduction

Conjugated polymers play an important role in materials science and are used in organic light-emitting diodes (OLEDS), solar cells, photovoltaic devices, field effect transistors, and lasers.[1−7] Poly(acetylene)s prepared from 1-alkynes have found limited application in the above-mentioned fields due to poor processing ability and stability upon oxidation; however, poly(acetylene)s derived from the cyclopolymerization of 1,6-heptadiynes[8−11] possess a conjugated backbone incorporated into the cyclic structures, thus providing enhanced stability and process ability, which can even be enhanced by cyclopolymerization of 4,4-disubstituted 1,6-heptadiynes.[12]

Since the discovery of 1,6-heptadiyne polymerization by means of Ziegler−Natta catalyst,[13] numerous cyclopolymerization studies leading to conjugated polymers with cyclic repeat units have been reported. However, in most cases, the use of Ziegler−Natta-type catalyst leads to the formation of insoluble polymer films.[14] Choi et al. found that Mo- and W-based catalytic systems are highly effective in the cyclopolymerization of 1,6-heptadiynes resulting in the selective formation of six-membered repeating units in polymer chain.[15−21] Schrock et al. demonstrated that well-defined, high oxidation state Mo-based initiators (e.g., Mo(*N*-2,6-$i\mathrm{Pr_2C_6H_3}$)($\mathrm{CHCMe_2Ph}$)($\mathrm{OCMe(CF_3)_2}$)$_2$) can be used for the living cyclopolymerization of diethyl dipropargylmalonate (DEDPM) and related derivatives;[22−23] however, the resulting polymers contain both five- and six-membered repeat units. Later, the same group demonstrated that dicarboxylate-derived catalysts, e.g., Mo(*N*-2-*t*-$\mathrm{BuC_6H_4}$)($\mathrm{CHCMe_3}$)($\mathrm{O_2CCPh_3}$)$_2$ can produce polyenes consisting exclusively of poly(cyclohex-1-ene-3-methylidene)s.[24] Our group reported on the living, stereo- and regioselective cyclopolymerization of selected 1,6-heptadiynes by various Mo-derived Schrock-type catalysts resulting in the selective formation of poly(1,2-cyclopent-1-enevinylene) units.[25−30] More recently, we were able to extend this chemistry to $\mathrm{Ru^{IV}}$-based metathesis catalysts.[31−32] With this chemistry in hand, conjugated polymers may now be prepared in air and in the presence of water.

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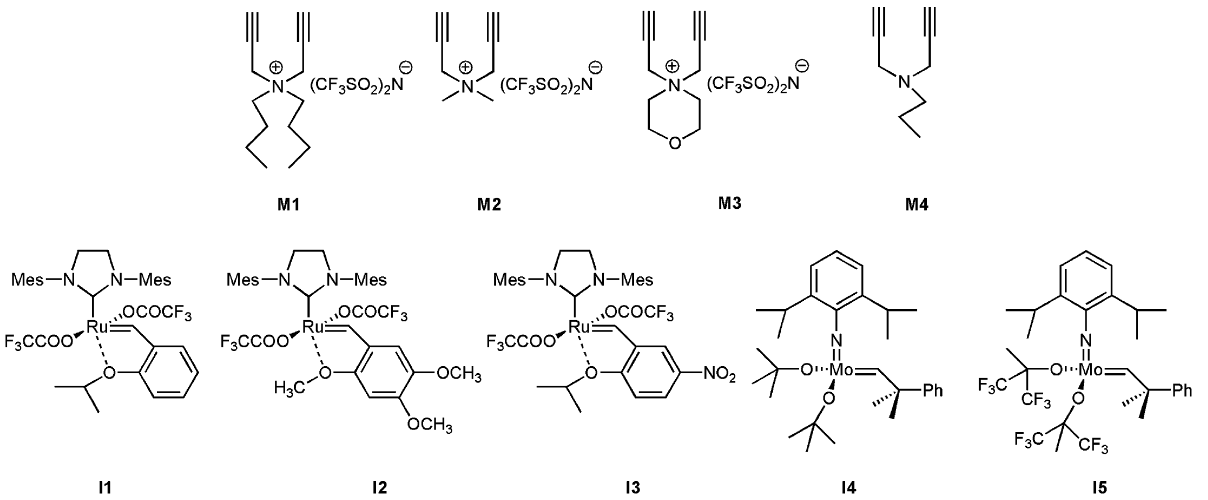
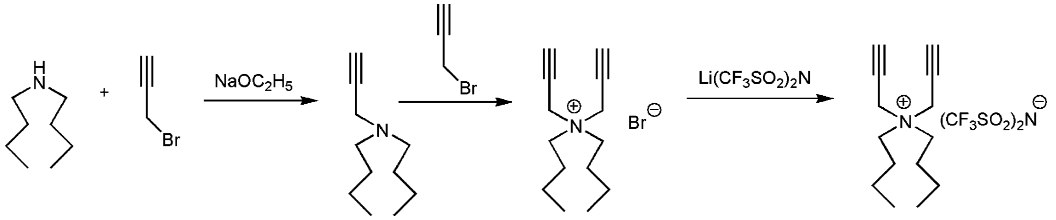


Figure 1. Structures of monomers **M1**−**M4** and initiators **I1**−**I5**. Mes = 2,4,6-trimethylphenyl.

Scheme 1. Monomer Synthesis



The cyclopolymerization of 1,6-heptadiynes carrying ionic moieties is a simple synthetic method for obtaining self-doped conjugated ionic polymers.[7] However, there are only few scattered reports on the cyclopolymerization of *ionic diynes*, which is related to the poor solubility of the latter in organic solvents and the deactivating effect of polar, ionic species on multicomponent, Lewis-acidic transition-metal halide catalysts.[33−35] Consequently, the relevant polymers obtained had low molecular weights, inherent viscosities ≤0.30 dL/g[33−35,39] or were found to be mostly insoluble.[36−39] As an alternative, the cyclopolymerization of *N*,*N*-dipropargyl-*N*-hexylamine by a Schrock initiator followed by quaternization with $CF_3SO_3CH_3$ has been elaborated.[40] Finally, the cyclopolymerization of 2-ethynyl-*N*-propargylpyridinum bromide was reported.[41] On the basis of our work dealing with the ring opening metathesis polymerization of ionic norbornene derivatives[42,43] and the cyclopolymerization of highly polar 1,6-heptadiynes[44] by means of specially designed Ru^{IV}-based initiators, we now present a comparative study for the cyclopolymerization of ionic *N*,*N*-dipropargyl-*N*,*N*-dialkyl ammonium bis(trifluoromethylsulfonyl)imides in different solvents and with various initiators.

Results and Discussion

In order to overcome the problems of monomer solubility as well as to increase the ionic conductivity of the resulting polymers, we chose bis(trifluoromethylsulfonyl)imide as a counteranion. Because of its fluorinated nature, this bulky anion is responsible for the solubility of the ionic monomers in organic solvents such as chloroform, dichloromethane, etc. In addition, as has already been demonstrated,[42−43] the bis(trifluoromethylsulfonyl)imide anion appears to be most inert under the action of ruthenium catalysts, thus permitting the synthesis of high molecular weight ionic polymers. Finally, our choice of the anion was defined by the fact, that polymers based on bis(trifluoromethylsulfonyl)imide are among those with the highest ionic conductivities.[45]

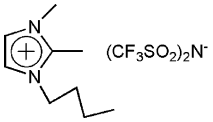
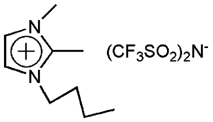
Monomer Synthesis. The synthesis of ionic *N*,*N*-dipropargylammonium salts was based on the subsequent alkylation[46]/quaternization reactions of the secondary amine (Scheme 1). The first step entailed the deprotonation of the corresponding amine with sodium ethanolate followed by alkylation using propargyl bromide. Depending on the amine, isolated yields were varied from 43 to 55%.

Quaternization was performed using conditions elaborated for the synthesis of high purity bromide-based ionic liquids (ILs),[47] which allowed for obtaining the pure, colorless monomer. Finally, the ion exchange process was accomplished according to published procedures.[48] In this final step, yields for **M1** and **M2** were 87 and 65%, respectively; however, due to the good solubility of **M3** in water, yields for this monomer were only around 30%. A summary of all monomers is given in Figure 1.

Polymer Synthesis. Trifluoroacetate-Derivatives of Grubbs-Type Initiators. The size of the substituent in the 4-position of a 1,6-heptadiyne plays an important role in the regio- and stereoselectivity of the polymerization. Thus, the substituents greatly influence both the resulting ring size and tacticity of the final polymer.[25−30,44] We started our investigations with the polymerization of **M1** having a polar, ionic nature and quite bulky alkyl side chains, which were anticipated to improve the solubility of the final polymer.[49] Polymerization of **M1** was first accomplished by the use of initiator **I1**[44] in chloroform (Table 1, entry 1). **I1** was chosen due to the simplicity of its preparation from commercially available $RuCl_2(IMesH_2)(2\text{-}(2\text{-}PrO{-}C_6H_4)$ as well as to the fact that cyclopolymerization of 1,6-heptadiynes with this catalyst results in the formation of highly conjugated polymers solely based on 1,2-(cyclopent-1-enylene)vinylenes.[44]

A rapid precipitation of the polymer from chloroform was observed. In due consequence, monomer conversion was comparably low (34%) and the obtained M_n was roughly 3.5 times smaller than the theoretical one. The polydispersity index was in the usual range for Ru−alkylidene triggered cyclopolymerizations (PDI = 1.37). It should be emphasized here, that

Table 1. Cyclopolymerization Results for M1−M3 by the Action of I1−I5 in Different Solvents[a]

#	solvent	monomer	[M]:[initiator]	initiator	T [°C]	yield [%][b]	λ_{max} [nm][c]	$M_{n\ theor.}$ [g/mol]	M_n [g/mol][d]	M_w [g/mol][d]	DP[e]	PDI[f]
1	$CHCl_3$	**M1**	1:100	**I1**	45	34	590	48 600	13 400	18 300	28	1.37
2		**M1**	1:100	**I1**	45	23	579	48 600	19 600	20 400	41	1.04
3		**M1**	1:100	**I1**	45	28	586	48 600	14 500	18 400	30	1.27
4		**M1**	1:100	**I1**	50	19	580	48 600	13 500	16 700	29	1.23
5		**M1**	1:100	**I1**	55	22	583	48 600	13 300	17 700	28	1.33
6		**M1**	1:100	**I2**	45	3	577	48 600	13 400	15 100	28	1.12
7		**M1**	1:100	**I3**	45	39	592	48 600	20 100	20 900	42	1.04
8		**M2**	1:100	**I1**	45	23	561	40 200	21 800	22 200	54	1.02
9		**M2**	1:100	**I3**	45	30	554	40 200	18 600	20 400	46	1.09
10		**M3**	1:100	**I3**	45	20	590	44 400	19 400	20 800	43	1.07
11	$CHCl_3$	**M2**	1:100	**I1**	45	25	586	40 200	18 700	20 900[g]	46	1.12
12	$CHCl_3$	**M2**	1:100	**I3**	45	37	589	40 200	19 300	21 300	48	1.10
13	$P^+(C_6H_{13})(C_{14}H_{29})\ (CF_3SO_2)_2N^-$	**M1**	1:100	**I1**	45	14	569	48 600	16 500	18 200	34	1.09
14	$N^+(C_6H_{13})(C_{14}H_{29})\ (CF_3SO_2)_2N^-$	**M1**	1:100	**I1**	45	7	564	48 600	16 900	18 700	35	1.11
15	CH_2Cl_2	**M2**	1:30	**I5**	25	96	559	12 100	16 300	16 900	41	1.03
16		**M2**	1:50	**I5**	25	97	555	20 100	17 800	18 400	44	1.03
17		**M2**	1:70	**I5**	25	97	553	28 100	18 300	18 400	46	1.01
18		**M2**	1:100	**I5**	25	95	-	40 200	20 500	21 400	51	1.05
19		**M2**	1:200	**I5**	25	86	556	80 100	19 500	20 300	49	1.04
20		**M2**	1:100	**I5**	25	38	592	40 200	17 700	19 200	44	1.08

[a] Reaction time 4 h, monomer concentration [M] = 1.0 mmol/g of solvent, catalyst concentration [Cat] = 7.8 mg/g of solvent. [b] Isolated polymer yields. [c] Measured in DMF. [d] GPC data measured in DMF. [e] Degree of polymerization. [f] Polydispersity index. [g] η_{inh} = 0.21 dL/g, for the solution of 0.05 g of polymer in 10.0 mL of DMFat 25.0 °C.

GPC measurements of ionic compounds were run in DMF and molecular weights were retrieved from calibration vs poly(styrene). Therefore, values for M_n and M_w obtained for ionic polymers must be discussed with some reservation.

In order to carry out a solution polymerization thus avoiding the problem of reduced molecular weights, cyclopolymerization of **M1** was performed in DMF. However, DMF in comparison to chloroform greatly decreased polymer yields. In search for alternative solvents, we turned our attention to ionic liquids (ILs).[50−57] Out of the large variety of ILs, 1,2-dimethyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide ($[1,2\text{-}Me_2\text{-}3\text{-}BuIm]^+(CF_3SO_2)_2N^-$) was chosen. As reported earlier,[42−43] this type of cation having a substituted C_2 atom proved itself as the best neutral solvent for the ring opening metathesis polymerization (ROMP) of different 2-norbornenes, including ionic ones. The bis(trifluoromethylsulfonyl)imide anion was chosen in order to expel the influence of possible ion exchange with the monomer[43] and because of the necessity to have an ionic, low viscosity solvent liquid at 45 °C. With this IL, the cyclopolymerization of **M1** by the action of **I1** was successfully performed (Table 1, entry 2). Though the precipitation of the polymer was observed as well, the degree of polymerization was higher than that obtained in chloroform. Moreover, PDIs were as low as 1.04. However, neither an increase in polymerization temperature, nor variations in concentration allowed for increasing polymer yields above 28% (Table 1, entries 3−5).

In an effort to further increase polymerization yields, a phosphonium based IL, which was found to be a superior solvent in the ROMP of 2-norbornenes by the action of ruthenium initiators, was used as an alternative solvent (Table 1, entry 13).[43] Replacement of the imidazolium based IL by a trihexyltetradecyl phosphonium bis(trifluoromethylsulfonyl)imide based one resulted in the formation of a polymer with a slightly higher molecular weight; however, isolated polymer yields decreased rather strongly. The same polymerization was also carried out in another aliphatic IL, i.e., in trihexyltetradecyl ammonium bis(trifluoromethylsulfonyl)imide, which is structurally quite similar to the ammonium monomer **M1** (Table 1, entry 14). The polymer was obtained with about the same molecular weight; however, polymer yields decreased as well.

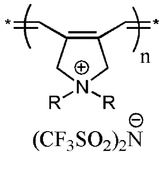
Since the establishment of $[RuCl_2(IMesH_2)_2({=}CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$ by Hoveyda et al. as a robust catalyst promoting olefin metathesis by a “release−return” mechanism,[58−59] different approaches to improve its catalytic reactivity were reported. Among these, changes in the electronic situation of the 2-isopropoxybenzylidene fragment are certainly among the most important ones.[60,61] Therefore, using the conditions elaborated above, polymerization of **M1** was carried out with initiators **I2** and **I3** (Table 1, entries 6 and 7). While **I2** was hardly able to cyclopolymerize **M1**, polymerization of this monomer in ($[1,2\text{-}Me_2\text{-}3\text{-}BuIm]^+(CF_3SO_2)_2N^-$) by the action of **I3** bearing the electron withdrawing nitro group allowed for increasing both the molecular weight and the isolated yield (39%, Table 1, entry 7). Thus, in accordance with the observations made by Grela et al.,[60,61] the decrease in electron density on the oxygen atom of the 2-propoxy fragment leads to an increase in cyclopolymerization activity. This observation illustrates the importance of initiation efficiency in these polymerizations.

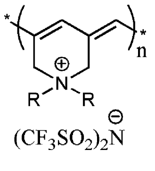
In principle, the low polymer yields may stem from poor initiator efficiency/activity or from thermally triggered degradation reactions of **M1**. Thus, thermally induced Hoffman degradation[50−57] of the quaternary ammonium salt would lead to the formation of a tertiary amine and a 1-olefin. While the tertiary amine may well be expected to slow down polymerization kinetics, the 1-olefin would not only act as a chain transfer agent thus leading to low molecular weights but also give raise to initiator decomposition. Therefore, we synthesized **M2** and tested it for the cyclopolymerization in both chloroform and the imidazolium-based IL. Indeed, polymerization of **M2** by the action of **I1** in $[1,2\text{-Me}_2\text{-3-BuIm}]^+(CF_3SO_2)_2N^-$ resulted in an increase in DP from 30 to 54 (Table 1, entry 8); however, isolated polymer yields were still around 25%. Implementation of the highly active initiator **I3** led only to insignificant changes in M_n and to polymer yields up to 30% (Table 1, entry 9). Similar results were obtained in chloroform (Table 1, entries 11 and 12). Finally, *N*,*N*-dipropargylmorpholinium bis(trifluoromethylsulfonyl)imide (**M3**) was subject to cyclopolymerization using **I3**. Though this monomer is insoluble in common organic solvents, both the aliphatic chains and the morpholinium moiety in **M3** are known to improve polymer solubility at least in ILs.[46,49,62,63] Despite the fact that precipitation of the polymer from the $[1,2\text{-Me}_2\text{-3-BuIm}]^+(CF_3SO_2)_2N^-$ solution was observed again and comparably low yields (20%) were obtained (Table 1, entry 10), this underlines the advantage of ILs, which allow for the polymerization of this monomer at least to a certain extent. As a matter of fact, monomer **M4** cannot be polymerized at all with Ru-based initiators even when highly active **I3** was used, strongly indicating that coordination of the nitrogen's lone pair to the Ru core effectively shuts down cyclopolymerization.

Schrock-Type Initiators. As an alternative to the bis(trifluoroacetate) modified Grubbs initiators, two Mo-based Schrock-type initiators, i.e., **I4** and **I5** were utilized (Figure 1). Monomer **M2**, which demonstrated the highest molecular weights and the highest yields in Ru-triggered cyclopolymerizations (*vide supra*) was chosen. In view of the high activity of Schrock initiators we found it somewhat surprising that **M2** may not be cyclopolymerized at all by the action of **I4**. However, the use of **I5** allowed for the formation of poly-**M2** in methylene chloride in high yields and with PDIs in the range of 1.01−1.05 (Table 1, entries 15−19), thus demonstrating the high reactivity and potential of this type of initiators.

Switching from methylene chloride to $[1,2\text{-Me}_2\text{-3-BuIm}](CF_3SO_2)_2N)$ (Table 1, entry 20) gave poor results in terms of polymer yields as well. While ILs have been reported to be useful solvents in Schrock catalyst triggered ring closing metathesis reactions,[64−65] they are apparently less useful solvents for cyclopolymerization. In terms of reactivity, it is worth mentioning that **M4** may be polymerized in $CHCl_3$ by **I5** in virtually quantitative yield, which is in accordance with ref 40 and again underlines the high reactivity of Schrock-type initiators. Unfortunately, due to the general insolubility of the polymer it was impossible to estimate its molecular weight and PDI.

Microstructure of Polymers. The cyclopolymerization of 1,6-heptadiynes by well-defined alkylidene complexes proceeds via α- or β-addition of one triple bond to the metal alkylidene, followed by cyclization, thus resulting in the formation of five- and six-membered repeat units.[22−23,40,66,67]





Classical binary and ternary $MoCl_5$- and WCl_6-based metathesis catalysts have been reported to form polymers solely based on six-membered repeat units with *N*,*N*-dipropargylammonium salts.[33−35] In contrast, the cyclopolymerizations of 1,6-heptadiynes catalyzed by Ru-based initiators in organic solvents resulted in polymers solely based on five membered ring structures.[44] We therefore turned our interest to the question, whether the selective formation of one single repeat unit by the action of Ru-based initiators would also apply to polar, N-containing, and ionic 1,6-heptadiynes. The structure of poly-**M1** obtained by the action of **I1** in either an IL or in chloroform was identified by FT-IR and ^1H and ^{13}C NMR spectroscopy. The ≡CH and C≡C stretching bands of **M1** at 3258 and 2133 cm^{-1}, respectively, had completely disappeared in the IR-spectrum of poly-**M1**.[33−35] In contrast to refs 33−35, we did not observe the C═C absorption band near 1650 cm^{-1}. Instead, the absorption band of the C═C stretching vibrations presented itself as a wide band with low-intensity masked by other bands in the 1650−1500 cm^{-1} region. In order to prove the presence of the conjugated double bonds, the Raman spectra of **M2** and poly-**M2** obtained by the action of **I3** and **I5**, respectively, were investigated. The Raman spectrum of **M2** displays bands at 2140 and 3298 cm^{-1}. These are attributed to the C≡C and −C≡CH vibrations. These bands completely disappeared in the Raman spectrum of poly-**M2** and two new bands at 1519 and 1553 cm^{-1} (for poly-**M2** obtained by the action of **I3**) as well as 1517 and 1548 cm^{-1} (for poly-**M2** obtained by the action of **I5**) that can be attributed to the conjugated double bonds were observed. In the ^1H NMR spectrum, the acetylenic protons of the monomer at 4.16 ppm disappeared, while new signals appeared at 6.0−7.0 ppm, attributed to the protons of the conjugated double bond. In the ^{13}C NMR spectrum, the olefinic carbon atom of poly-**M1** appeared at 130−135 ppm, whereas the acetylenic carbon peaks of the monomer at 72 and 83 ppm completely disappeared. Most important, apart from the signal for the CF_3-group, 7 signals *only* attributable to a 5-membered repeat unit were observed. In addition, the chemical shifts of C-6 and C-5 agree well with monomeric model compounds, e.g., *N*,*N*-dibutyl-2,5-dihydropyrrolium salts. Thus, on the basis of these data and the signal: noise ratio for C-2, C-3 (Figure 2) it can be concluded that poly-**M1** consists of *at least* 95% 5-membered repeat units, i.e., (3,4-(1*H*-2,5-dihydropyrrolylene)-vinylene)s along the conjugated backbone.

Similar observations were made for poly-**M2** and poly-**M3** synthesized by action of any of the Ru−bis(trifluoroacetate)-derived initiators (**I1**−**I3**) (Figure 3), irrespective of the solvent used, confirming previous reports that *Ru-based initiators promote the cyclopolymerization of 1,6-heptadiynes*[31−32,44] *and apparently also of dipropargylammonium salts via selective α-addition.* In contrast, poly-**M2** synthesized by the action of the Schrock initiator **I5** (cf. Figure 3) was found to consist of both 5- and 6-membered ring units, i.e., (3,4-(1*H*-2,5-dihydropyrrolylene)vinylene)s and (3,5-(1,2,5,6-tetrahydropyridinylene)-methylidene)s. Quantitative analysis of the carbonyl and proton resonances revealed a ratio of five- to six-membered rings of approximately 7:3, irrespective of the reaction medium used, which correlates with earlier results obtained with Schrock-type initiators.[22−23]

UV Spectra and Solvatochromic Behavior. UV−vis data for all polymers prepared are summarized in Table 1. Poly-**M1** displayed solvatochromic behavior. Thus, values for λ_{max} changed in the following order: DMSO (596 nm) > dimethylacetamide (588 nm) > dimethylformamide (DMF, 579 nm) > acetone (570 nm) > acetonitrile (567 nm) > *N*-methylpyrrolidone (504 nm).

This difference in λ_{max} of up to 93 nm can be explained by specific solvation effects. Interestingly, the presence of water in DMF leads to the appearance of a second band at 550 nm (Table 2). In fact, these solutions of poly-**M1** in DMF turned out to be extremely sensitive toward traces of water. Thus, addition of even 0.55 − 0.68 wt % water led to a change in absorption maximum of 7 nm *and the appearance of a second*

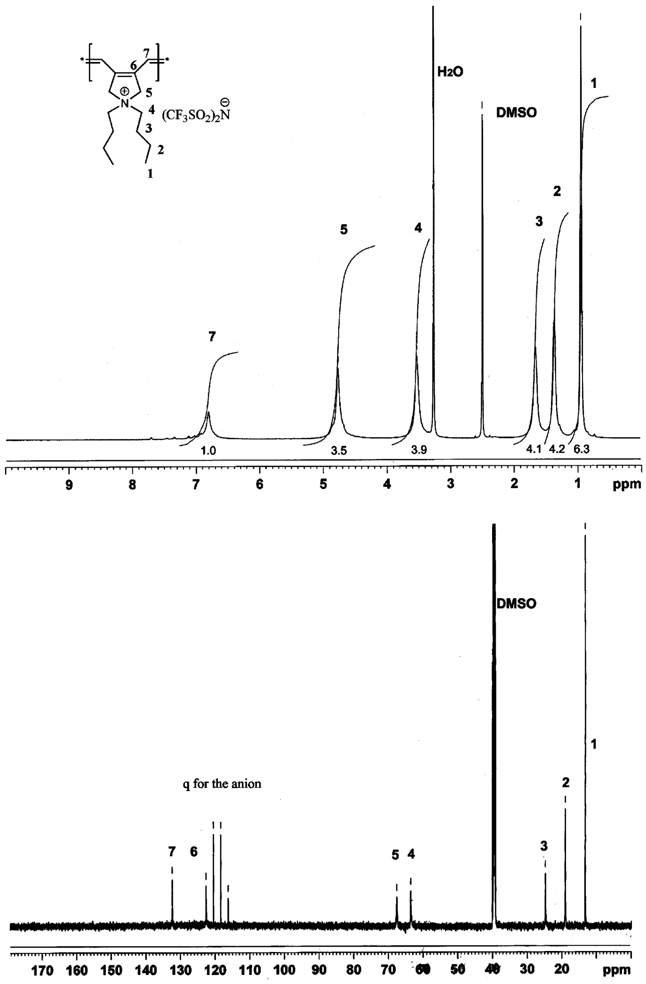


Figure 2. ^{1}H and ^{13}C NMR spectra of poly-**M1** prepared by the action of **I1**.

maximum at 541 nm (Figure 4). In order to explain the presence of two bands, some complementary experiments were carried out. Thus, NEt_3 and acetic acid, respectively, were added to a solution of poly-**M1** in DMF. While the addition of NEt_3 leads to the transformation of the two maxima in a water containing polymer solution into one single maximum at $\lambda_{max} = 580$ nm, the addition of acetic acid to the polymer solution in dry DMF caused the appearance of the three absorption bands with absorption maxima at 507, 543, and 583 nm, respectively. We therefore conclude that both water and acetic acid can solvate the polymer chain via hydrogen bond formation, leading to the formation of new bands, while NEt_3 as a proton acceptor destroys these hydrogen bonds and restores the system in its original state with one single maximum. Hydrogen bonding might be expected to lead to a specific solvation of some separate polymer chain regions[76] and therefore to the violation of conjugation and planarity. The change in the polymer order and the partial loss of its conjugation results in the appearance of new absorption bands shifted to shorter wavelengths, which is in a full agreement with theory.[68]

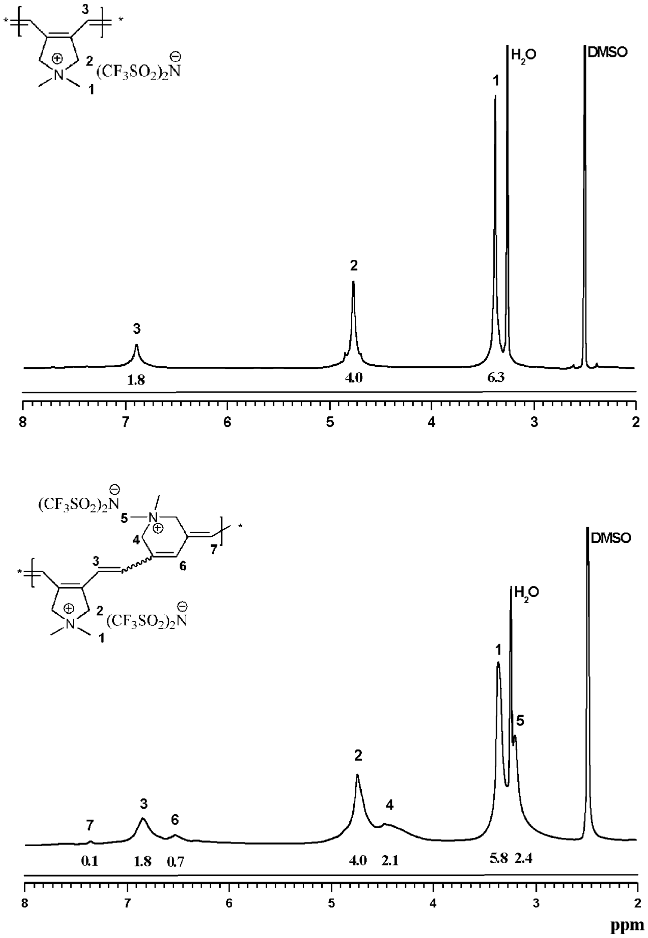


Figure 3. ^{1}H NMR spectra of poly-**M2** prepared by the action of **I1** and **I5,** respectively.

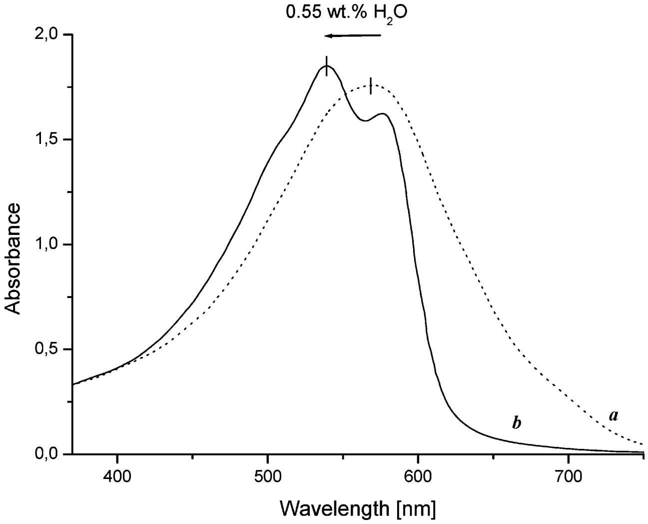


Figure 4. UV spectra of poly-**M1** in DMF (a) and in DMF with water added (b) (polymer mass 0.00010 g, $V_{DMF} = 3$ mL).

Polymer Properties. Poly-**M1**, poly-**M2**, and poly-**M3** are stable under ambient conditions. No observable changes in the UV, IR, or NMR spectra were observed within 2 months. In contrast, purple poly-**M4** was air sensitive and turned dark brown only 15 min after exposure to air. Apparently, quaternization stabilizes the conjugated backbone.[34] Due to the bis(trifluoromethylsulfonyl)imide anion, poly-**M1**, poly-**M2**, and poly-**M3** were soluble in common polar amide organic solvents such as DMF, DMSO, DMAA, and NMP, partly soluble in acetone, and, upon gentle warming, soluble in acetonitrile (!). As mentioned, poly-**M4** resembles poly(*N*,*N*-dipropargylaniline)[30] and was insoluble in any solvent with the exception of strong organic acids capable of forming the corresponding poly(ammonium) salt.

TMA measurements revealed that poly-**M1** prepared by the action of **I3** had a glass transition temperature (T_g) of 79°C, while poly-**M2** did not show any T_g, neither in TMA nor in DSC (Table 3).

Table 2. Changes in UV Spectrum of Poly-M1 in DMF upon Addition of Water[a]

		amount of water added	
λ_{1max} [nm]	λ_{2max} [nm]	[μL]	[wt %]
571			
574		5	0.17
580		10	0.34
578		15	0.51
581	551	20	0.68
580	549	25	0.85
581	545	30	1.02
580	545	35	1.19
579	542	40	1.36
578	541	50	1.70

[a] Polymer mass 0.0001 g, $V_{DMF} = 3$ m*L* $= 3030$ μL.

This is attributed to the presence of the butyl chains in **M1**, which on the one hand are plasticizing the polymer chain and on the other hand decrease packing density. Interestingly, **I5**-derived poly-**M2** containing both five- and six-membered rings (Table 3, entry 3) displayed a T_g in the same region as poly-**M1** solely based on 5-membered repeat units despite the fact that the presence of 6-membered ring units also affects both packing density and rigidity of the polymer chain.

The thermal stability of poly-**M1**, poly-**M2**, and poly-**M3** was studied by TGA (Table 3). No significant difference in the thermal resistance of the polymers was found. Degradation temperatures of 200−230 °C were found for poly-**M1**, poly-**M2**, and poly-**M3**. However, replacing the alkyl chains by cyclic structures, i.e., changing from monomer **M1** to **M3**, led to a moderate increase in polymer thermal stability by 40 °C. In view of the thermal resistance of poly(dihexyldipropargylammonium bromide) and poly(dihexyldipropargylammonium tosylate) (initial weight loss is at 150 °C and 170 °C, respectively[33]), it can be concluded that the thermal stability of ionic poly(1,6-heptadiyne)s is rather determined by the anion than by variations in the side chains.

Poly(1,6-heptadiyne) films obtained from DMF solutions were brittle, irrespective of the molecular weights and initial monomer (**M1**−**M3**). It is worth mentioning that coatings on a metal foil were brittle as well, however, coatings on a glass support were rather durable even to the abrasion. An increase in DP from 10−14[33] to 48−54 did not affect the tough properties of the resulting films. To check for any crystalline domains, X-ray diffraction experiments were carried out. It was found that all the polymers powders were amorphous. Thus, the impossibility of self-supporting film formation was assigned to the rigidity of the conjugated polymer backbone and to its comparably low molecular weights. In order to further improve toughness, blends of poly-**M1** were formulated. As a second constituent, poly(*N*-vinylethylimidazolium dicyanamide) (poly([ViEtIm]N(CN)$_2$), $M_z = 1\,130\,000$ g/mol)[45] was chosen because of its capability of forming elastic, durable films as well as because of its good conductivity. As a result of blending, self-supporting, tough films were obtained using a weight ratio 50:50 for poly-**M1** and poly([ViEtIm]N(CN)$_2$). Ionic conductivity measurements (Figure 5, Table 3) revealed that at lower frequencies, the conductivity of the blended polymer films was lower then of the original poly([ViEtIm]N(CN)$_2$); however, at higher frequencies, the differences vanished and polymer blends partly based on either poly-**M1** or poly-**M3** had a *higher* conductivity than a pure poly([ViEtIm]N(CN)$_2$) film. We do not exclusively attribute this fact to anion oscillation, but also tentatively to the contribution of conductivity resulting from a $\pi \rightarrow \pi^*$ electron transfer through the conjugated polymer backbone. It is further noticeable that one can observe the differences between the conductivity of a polymer consisting solely of five-membered ring structures and a polymer based on the mixture of six- and five-membered rings.

The appearance of the curves is similar; however, the conductivity values differ by 1 order of magnitude. This superior conductivity is in agreement with previous measurements on poly(diethyldipropargyl malonate) films. Thus, poly(diethyldipropargyl malonate) films solely consisting of 5-membered ring structures displayed a *higher* conductivity than those consisting of a mixture of 5- and 6-membered ring structures.[69] Concomitantly, an increased degree of conjugation in polyenes solely consisting of 5-membered ring structures—as reflected by their higher UV−vis absorption maxima—was observed.[25−32] Since the ionic conductivity of the polymer blend at high frequencies exceeds that of pure poly([ViEtIm]N(CN)$_2$), one can estimate that the conductivity of poly-**M1** and poly-**M3**, respectively, must be in the range of 10^{-6}−10^{-5} S/cm, which would be several orders of magnitude higher than that for previously known analogues of this type.[33−35,40]

Experimental Section

General Procedures and Materials. All manipulations were performed under an argon atmosphere by standard Schlenk techniques or under a nitrogen atmosphere in an MBraun drybox (Garching, Germany). Experimental Details on chemicals are given elsewhere.[43] All ruthenium-based initiators **I1**−**I4** (Figure 1) were synthesized via reaction of the parent dichlorocomplexes with a twofold excess of silver trifluoroacetate, as described in a previous paper.[70] [RuCl$_2$(IMesH$_2$)$_2$(=CH-2-(2-PrO)C$_6$H$_4$)] was commercially purchased and used without any purification. [Ru(CF$_3$CO$_2$)$_2$-(IMesH$_2$)$_2$(=CH-2-(2-PrO)C$_6$H$_4$)] (**I1**),[70] [Ru(CF$_3$CO$_2$)$_2$(IMesH$_2$)$_2$-(=CH-2,4,5-(OMe)$_3$C$_6$H$_2$)] (**I2**),[31,61] and [Ru(CF$_3$CO$_2$)$_2$ (IMesH$_2$)$_2$-(=CH-2-(2-PrO)-5-NO$_2$C$_6$H$_4$)] (**I3**)[71,72] as well as Mo(*N*-2,6-*i*Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(O-*t*Bu)$_2$ (**I4**) and Mo(*N*-2,6-*i*Pr$_2$C$_6$H$_3$)-(CHCMe$_2$Ph)(OC(CH$_3$)(CF$_3$)$_2$)$_2$[73] (**I5**) were prepared according to published procedures.

Inherent viscosities (η_{inh})were measured using an Ostwald capillary viscometer (0.05 g of polymer in 10.0 mL of DMF at 25.0 °C). Molecular weights and polydispersity indexes (PDIs) of the polymers were determined by gel permeation chromatography (GPC) on 3 consecutive Waters Styragel HR4 4.6 × 300 mm columns in DMF at 30 °C using an isocratic pump 1515, an Autosampler 1717 and a 2415 refractive index (RI) detector (All Waters Co, USA). The flow rate was set to 1 mL·min^{-1}. Narrow poly(styrene) standards in the range $162 < M_n < 6\,035\,000$ g·mol^{-1} (Easi Vial-red, yellow and green) were purchased from Polymer Labs. NMR data were obtained at 600.25 MHz for proton and 150.94 MHz for carbon in the indicated solvent at 25 °C on a Bruker Avance^{II+} 600 and are listed in ppm downfield from tetramethylsilane for proton and carbon. ^{19}F NMR spectra were measured on a Bruker AMX-300 spectrometer with 282.40 MHz working frequency. IR spectra were recorded on a Bruker Vector 22 using ATR technology. UV measurements were performed on a UV−vis scanning spectrometer (Shimadzu UV-2101 PC) in 10 mm cells. GC−MS investigations were carried out on a Shimadzu GCMS-QP5050, using a SPB-5 fused silica column (30 m × 0.25 μm film thickness). Dynamic thermogravimetric analysis (TGA) was performed in air on a TGA7 Perkin-Elmer applying a heating rate of 10 °C/min. DSC data for monomers were recorded by heating under a nitrogen atmosphere on a DSC7 Perkin-Elmer differential scanning calorimeter. The glass transition temperature (T_g) of the polymers was determined by thermomechanical method using a UIP-70 M (Russia) thermomechanical analyzer at a heating rate of 2.5°C min^{-1}. High-resolution mass spectra (HRMS) measured by means of electron spray ionization (ESI) were recorded on a FT-ICR-MS Bruker Daltonics APEX II.

Conductivity Measurements. Dielectric spectroscopy studies were run on a Novocontrol Broadband Dielectric spectrometer equipped with an Alpha analyzer and a Quatro temperature

Table 3. Polymer Properties of Poly-M1- Poly-M3

					conductivity (σ) [S·cm^{-1}][c]at 20 °C			
monomer/initiator	M_n [g/mol][a]	T_{onset} [°C][b]	$T_{5\%}$ [°C][b]	T_g [°C]	50[d] Hz	10^3 Hz	10^6 Hz	10^7 Hz
poly-**M1**/**I3**	20 100	230	280	79	2.32×10^{-8}	8.86×10^{-8}	1.53×10^{-5}	3.89×10^{-5}
poly-**M2**/**I3**	19 300	200	280	*e*	2.96×10^{-8}	1.17×10^{-7}	1.78×10^{-6}	5.76×10^{-6}
poly-**M2**/**I5**	20 500	210	280	70	8.78×10^{-9}	2.14×10^{-8}	3.98×10^{-7}	1.64×10^{-6}
poly-**M3**/**I3**	19 400	240	290	*f*	2.15×10^{-7}	8.13×10^{-7}	1.59×10^{-5}	3.46×10^{-5}
poly([ViEtIm]N(CN)$_2$)	1130000[g]	170	230	19	2.09×10^{-6}	5.30×10^{-6}	1.51×10^{-5}	2.84×10^{-5}

[a] GPC data measured in DMF. [b] Onset and 5% weight loss temperature according to TGA. [c] Conductivity of self-standing films prepared from 50 wt % blends with poly(ViEtIm)N(CN)$_2$ at 20 °C. [d] Working frequency *f*. [e] No T_g was determined either by thermomechanical method or by DSC. [f] Not determined. [g] M_z was measured by sedimentation method in NMP.

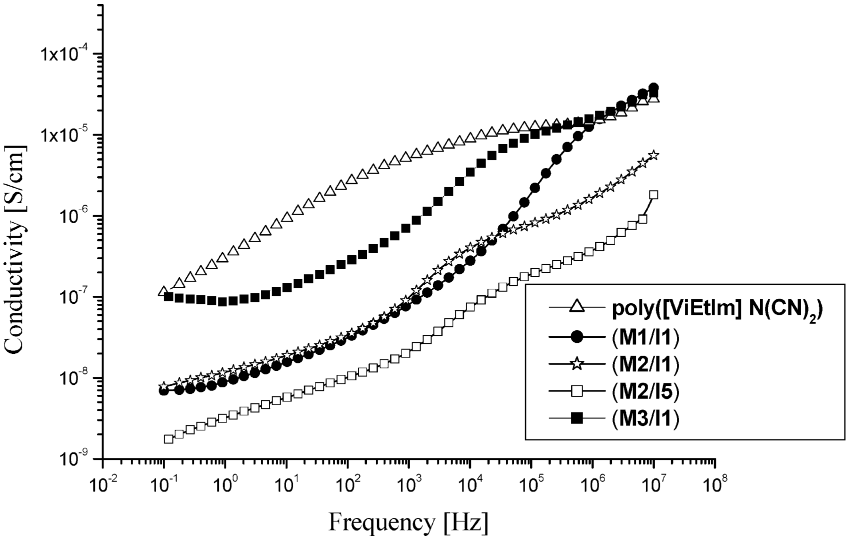


Figure 5. Ionic conductivity of self-supporting films based on poly([ViEtIm]N(CN)$_2$)/poly(1,6-heptadiyne) bis(trifluoromethylsulfonyl)imides as a function of frequency applied ($T = 25$ °C).

controller. The films were sandwiched between the gold-coated brass electrodes. The experiments were carried out isothermally increasing the temperature from 20 to 50°C in 10 °C steps in the $10^{-1}-10^{7}$ Hz frequency range.

Film Preparation. Blending the various poly(1,6-heptadiyne)s with poly(vinylethylimidazolium dicyanamide) (poly([ViEtIm]N(CN)$_2$), $M_z = 1\,130\,000$ g/mol, prepared according to ref 45) was completed within 2 h by vigorous stirring in DMF (weight ratio was 50/50). Films of the polymer blends were cast from a 5% polymer solution on clean Teflon supports followed by slow solvent evaporation at 80−90°C. Final drying was carried out *in vacuo* at 45 °C for 12 h.

Ionic Liquids (ILs). Imidazolium-based ILs used in this study were prepared in accordance with published procedures[46−48,62] and characterized by elemental analysis, NMR and IR spectroscopy. Trihexyl(tetradecyl)phosphonium chloride was a gift from Cytec Inc. Trihexyl(tetradecyl)ammonium bromide was purchased from Fluka and used as received.

Trihexyl(tetradecyl)ammonium Bis(trifluoromethylsulfonyl)imide. The compound was prepared according to ref 74 with some minor changes. A solution of lithium bis(trifluoromethylsulfonyl)imide (5.0 g, 0.017 mol) dissolved in 50 mL of dry acetone was added dropwise to a solution of trihexyl(tetradecyl)ammonium bromide (8.0 g, 0.014 mol) in 100 mL of acetone. Stirring was continued for 5 h at ambient temperature. The solution was evaporated and the resulting viscous, slightly yellow oil was redissolved in 200 mL of diethyl ether. The ether layer was thoroughly washed with water and then dried over sodium sulfate. Again, the diethyl ether was stripped off and the product was dried *in vacuo* at 55 °C with a flask filled with P_2O_5 introduced into the vacuum line. Yield: 75%. ^{1}H NMR (CDCl$_3$): $\delta = 3.17-3.12$ (m, 8H), 1.6 (m, 8H), 1.35−1.28 (m, 40H), 0.93−0.89 (m, 12H). ^{13}C NMR (CDCl$_3$): $\delta = 126.1-113.3$ (q, anion, $J_{CF} = 321.8$ Hz), 58.3, 31.7, 30.8, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.7, 25.8, 25.5, 22.4, 22.1, 21.4, 13.8, 13.5. ^{19}F NMR (CDCl$_3$): $\delta = -78.82$. Anal. Calcd for $C_{34}H_{68}F_6S_2O_4N_2$: C, 54.66; H, 9.17; F, 15.26. Found: C, 54.42; H, 9.02; F, 15.28.

Trihexyl(tetradecyl)phosphonium Bis(trifluoromethylsulfonyl)imide. The compound was synthesized according to ref 74. Yield: 79%. ^{31}P NMR (CDCl$_3$): $\delta = 32.96$. ^{19}F NMR (CDCl$_3$): $\delta = -78.84$. Anal. Calcd for $C_{34}H_{68}F_6S_2O_4NP$: C, 53.45; H, 8.97; F, 14.92; P, 4.05. Found: C, 53.41; H, 8.96; F, 15.25; P, 4.03.

***N,N*-Dibutyl-*N*-propargylamine.** Freshly dried ethanol (100 mL) was charged into a three necked flask equipped with a $CaCl_2$ tube and an inert inlet. Sodium (2.76 g, 0.119 mol) was then slowly dissolved in portions. After the dissolution of the last portion, the reaction mixture was stirred at room temperature for 30 min; then a solution of di-*n*-butylamine (15.45 g, 0.119 mol) in 20 mL of absolute ethanol was added dropwise under an inert flow. Again the reaction mixture was stirred for 1 h at ambient temperature and then cooled to 0 °C in an ice bath. Propargyl bromide (10.36 mL, 0.119 mol) was slowly added. The mixture was stirred at 0 °C for 2 h and at 20 °C for 12 h and finally at 50 °C for 1 h. The mixture was then filtered and ethanol was evaporated yielding an orange oil, which was distilled under reduced pressure. The final product was a colorless transparent liquid with a typical amine odor. Yield: 8.61 g (43%). ^{1}H NMR (CDCl$_3$): $\delta = 3.44$ (d, 2H, $J_{HH} = 2.3$ Hz, $N-CH_2-C{\equiv}CH$), 2.65−2.61 (t, 2H, $J_{HH} = 7.2$ Hz, $N-CH_2-CH_2$), 2.51−2.47 (t, 2H, $J_{HH} = 7.3$ Hz, $N-CH_2-CH_2$), 2.19−2.18 (t, 1H, $J_{HH} = 2.3$ Hz, $N-CH_2-C{\equiv}CH$), 1.5−1.35 (m, 8H), 0.98−0.93 (t, 6H, $J_{HH} = 7.2$ Hz, $-CH_2-CH_3$). ^{13}C NMR (CDCl$_3$): $\delta = 78.8$, 72.4, 53.4, 49.8, 41.7, 32.3, 29.7, 20.6, 14.8, 14.0, 13.2. IR (ATR mode): 3452 (w), 3311 (vs), 3206 (m), 2958 (vs), 2932 (vs), 2862 (vs), 2873 (vs), 2820 (m), 2118 (sm, $\upsilon_{C\equiv C}$), 1686 (w), 1653 (w), 1616 (w), 1467 (vs), 1459 (vs), 1378 (s), 1324 (s), 1240 (m), 1180 (m), 1144 (s), 1129 (s), 1094 (vs), 1045 (m), 950 (m), 934 (m), 900 (s), 735 (s), 647 (vs), 623 (vs) cm^{-1}.

***N,N*-Dibutyl-*N,N*-dipropargylammonium Bromide.** This monomer was synthesized similarly to the imidazolium bromide based IL.[47,75] A solution of *N,N*-dibutyl-*N*-propargyl amine (8.6 g, 0.052

mol) in 50 mL of dry chloroform was cooled in an ice bath to 0 °C. After 30 min, an excess of propargyl bromide (5.8 mL, 0.067 mol) was added very slowly to the intensively stirred reaction mixture. The reaction mixture was kept at 0 °C for 24 h under stirring and inert atmosphere. Then the temperature was stepwise risen to 25 °C for 12 h and finally to 40 °C for 12 h. Chloroform and excess propargyl bromide were removed by distillation under reduced pressure and the resultant viscous liquid was treated with dry *n*-hexane in order to remove the impurities. Finally, the yellow solid residue was crystallized from dichloromethane/benzene to yield white crystals, which were dried at 50 °C for 8 h *in vacuo* with a flask filled with P_2O_5 introduced into the vacuum line. Yield: 10.5 g (72%). Mp = 136.7 °C. ^{1}H NMR (DMSO-d_6): δ = 4.5 (s, 4H, $\mathrm{N{-}}\mathit{CH}_2\mathrm{{-}C{\equiv}CH}$), 4.16−4.15 (d, 2H, J_{HH} = 1.6 Hz, $\mathrm{N{-}CH_2{-}C{\equiv}}\mathit{CH}$), 3.46−3.39 (m, 4H, $\mathrm{N{-}}\mathit{CH}_2\mathrm{{-}CH_2}$), 1.72−1.70 (m, 4H, $\mathrm{N{-}CH_2{-}}\mathit{CH}_2$), 1.39−1.32 (m, 4H, $\mathrm{N{-}CH_2{-}CH_2{-}}\mathit{CH}_2$), 0.98−0.93 (t, 6H, J_{HH} = 7.3 Hz, $\mathrm{{-}CH_2{-}}\mathit{CH}_3$). ^{13}C NMR (DMSO-$d_6$): δ = 83.8, 72.1, 59.7, 49.9, 23.9, 19.6, 13.9. IR (ATR mode): 3426 (w), 3122 (vs), 2960 (vs), 2928 (s), 2874 (m) 2116 (vs, $\upsilon_{\mathrm{C\equiv C}}$), 1563 (w), 1467 (vs) 1446 (m), 1416 (m), 1377 (m), 1349 (w), 1165 (w), 1149 (w), 1129 (w), 1062 (w), 1041 (m), 1023 (sw), 968 (w), 957 (w), 860 (s), 790 (m), 734 (m), 619 (w), 433 (w) cm^{-1}. Anal. Calcd for $C_{14}H_{24}NBr$: C, 58.74; H, 8.45; N, 4.89. Found: C, 58.84; H, 8.54; N, 4.88.

***N,N*-Dibutyl-*N,N*-dipropargylammonium Bis(trifluoromethylsulfonyl)imide (M1).** Ion exchange was performed in the same way as described for the ILs.[48] To a solution of *N,N*-dibutyl-*N,N*-dipropargylammonium bromide (4.0 g, 0.014 mol) in 15 mL of distilled water a solution of $\mathrm{Li(CF_3SO_2)_2N}$ (3.7 g, 0.013 mol) in 15 mL of water was added dropwise. Stirring was continued for 1 h at ambient temperature and for 1 h at 45 °C. Then, 25 mL of dichloromethane were added to the resultant emulsion, the dichloromethane fraction was thoroughly washed with water (5 × 40 mL) and dried over sodium sulfate. The solvent was evaporated and the solid, colorless product was dried *in vacuo* at 50 °C for 12 h with a flask filled with P_2O_5 introduced into the vacuum line. Yield: 5.4 g (87%). Mp = 40.4 °C. ^{1}H NMR (DMSO-d_6): δ = 4.39−4.38 (d, 4H, J_{HH} = 5.4 Hz, $\mathrm{N{-}}\mathit{CH}_2\mathrm{{-}C{\equiv}CH}$), 4.01−4.00 (d, 2H, J_{HH} = 3.0 Hz, $\mathrm{N{-}CH_2{-}C{\equiv}}\mathit{CH}$), 3.41−3.35 (m, 4H, $\mathrm{N{-}}\mathit{CH}_2\mathrm{{-}CH_2}$), 1.76−1.63 (m, 4H, $\mathrm{N{-}CH_2{-}}\mathit{CH}_2$), 1.39−1.31 (m, 4H, $\mathrm{N{-}CH_2{-}CH_2{-}}\mathit{CH}_2$), 0.98−0.92 (t, 6H, J_{HH} = 17.4 Hz, $\mathrm{{-}CH_2{-}}\mathit{CH}_3$). ^{13}C NMR (DMSO-$d_6$): δ = 122.6−116.2 (q, anion, J_{CF} = 322.0 Hz), 83.2, 71.4, 59.2, 49.3, 23.3, 18.9, 13.1. IR (ATR mode): 3258 (m), 2973 (w), 2881 (w), 2133 (w), 1473 (m), 1388 (s, ν_{CF}), 1347 (s, $\nu_{\mathrm{asSO_2}}$), 1179 (vs, ν_{CF}), 1138 (s, $\nu_{\mathrm{sSO_2}}$), 1048 (vs), 969 (w), 901 (m), 856 (m), 790 (m), 761 (m), 738 (m), 611 (vs), 580 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{24}F_6S_2O_4N_2$: C, 39.50; H, 4.97; N, 5.76. Found: C, 39.56; H, 4.94; N, 5.74. All intermediates in the synthesis of **M2** and **M3** as well as the final monomers were prepared in a similar way and characterized by elemental analysis, NMR, and IR spectroscopy.

***N,N*-Dimethyl-*N,N*-dipropargylammonium Bis(trifluoromethylsulfonyl)imide (M2).** Yield: 65%; Mp = 49.1 °C. ^{1}H NMR (DMSO-d_6): δ = 4.40−4.39 (d, 4H, J_{HH} = 2.4 MHz, $\mathrm{N{-}}\mathit{CH}_2\mathrm{{-}C{\equiv}CH}$), 4.05−4.03 (t, 2H, J_{HH} = 3.0 MHz, $\mathrm{CH_2{-}C{\equiv}}\mathit{CH}$), 3.15 (s, 6H, $\mathrm{{-}N{-}(}\mathit{CH}_3\mathrm{)_2}$). ^{13}C NMR (DMSO-$d_6$): δ = 122.6−116.2 (q, anion, J_{CF} = 322.0 Hz), 83.3, 71.6, 53.3, 49.7. IR (ATR mode): 3288 (m), 3041 (w), 2998 (w), 2965 (w), 2138 (m), 1478 (m), 1459 (m), 1425 (m), 1346 (vs, ν_{CF}), 1326 (vs, $\nu_{\mathrm{asSO_2}}$), 1176 (vs, ν_{CF}), 1136 (vs, $\nu_{\mathrm{sSO_2}}$), 1048 (vs), 1036 (vs), 1015 (s), 983 (m), 951 (m), 893 (m), 878 (s), 792 (m), 765 (w), 741 (m), 710 (s), 672 (vs), 610 (vs) cm^{-1}. Raman, $\Delta\nu$: 3485 (w), 3439 (w), 3298 (w, $\nu_{\mathrm{-C\equiv CH}}$), 3217 (w), 3042 (w), 2968 (m), 2686 (w), 2140 (vs, $\nu_{\mathrm{C\equiv C}}$), 1627 (w), 1422 (w), 1201 (w), 1091 (m), 953 (w), 916 (w), 845 (w), 727 (s), 707 (vs), 606 (w), 548 (w), 363 (m), 305 (s), 272 (vs), 230 (s), 121 (s), 54 (m) cm^{-1}. Anal. Calcd for $C_{10}H_{12}F_6S_2O_4N_2$: C, 29.85; H, 3.01; N, 6.96. Found: C, 29.61; H, 2.98; N, 7.04.

***N,N*-Dipropargylmorpholinium Bis(trifluoromethylsulfonyl)imide (M3).** Yield: 30%. Mp = 77.8 °C. ^{1}H NMR (DMSO-d_6): δ = 4.62−4.61 (d, 4H, J_{HH} = 2.4 MHz, $\mathrm{N{-}}\mathit{CH}_2\mathrm{{-}C{\equiv}CH}$), 4.09−4.08 (t, 2H, J_{HH} = 2.4 MHz, $\mathrm{CH_2{-}C{\equiv}}\mathit{CH}$), 3.98−3.97 (t, 4H, J_{HH} = 4.9 MHz, $\mathrm{{-}N{-}}\mathit{CH}_2\mathrm{{-}CH_2{-}O{-}}$), 3.58−3.57 (t, 4H, J_{HH} = 4.9 MHz, $\mathrm{{-}N{-}CH_2{-}}\mathit{CH}_2\mathrm{{-}O{-}}$). ^{13}C NMR (DMSO-$d_6$): δ = 122.5−116.2 (q, anion, J_{CF} = 321.9 Hz), 83.8, 70.8, 59.4, 56.7, 49.9. IR (ATR mode): 3293 (m), 3270 (m), 3025 (w), 2994 (w), 2966 (w), 2891 (w), 2132 (m), 1466 (m), 1441 (m), 1345 (vs, ν_{CF}), 1327 (vs, $\nu_{\mathrm{asSO_2}}$), 1262 (w), 1199 (s), 1181 (vs, ν_{CF}), 1126 (s, $\nu_{\mathrm{sSO_2}}$), 1050 (vs), 1010 (s), 993 (s), 968 (m), 944 (m), 877 (s), 796 (m), 762 (m), 739 (m), 694 (s), 674 (s), 607 (vs) cm^{-1}. Anal. Calcd for $C_{12}H_{14}F_6S_2O_5N_2$: C, 32.44; H, 3.18; N, 6.30. Found: C, 31.41; H, 2.98; N, 6.15.

***N*-Propyl-*N,N*-dipropargylamine (M4).** The compound was synthesized according to a published procedure.[35] ^{1}H NMR ($CDCl_3$): δ = 3.40−3.39 (d, 4H, J_{HH} = 2.4 MHz, $\mathrm{N{-}}\mathit{CH}_2\mathrm{{-}C{\equiv}CH}$), 2.46−2.43 (t, J_{HH} = 7.2 Hz, 2H, $\mathrm{N{-}}\mathit{CH}_2\mathrm{{-}CH_2{-}CH_3}$), 2.19−2.18 (t, J_{HH} = 4.8 Hz, 2H, $\mathrm{N{-}CH_2{-}C{\equiv}}\mathit{CH}$), 1.49−1.43 (m, J_{HH} = 7.2 Hz, 2H, $\mathrm{N{-}CH_2{-}}\mathit{CH}_2\mathrm{{-}CH_3}$), 0.89−0.87 (t, J = 7.2 Hz, 3H, $\mathrm{N{-}CH_2{-}CH_2{-}}\mathit{CH}_3$). ^{13}C NMR ($CDCl_3$): δ = 78.9, 72.9, 54.9, 42.1, 20.7, 11.8. IR (ATR mode): 3295 (vs), 2960 (s), 2933 (s), 2874 (m), 2817 (m), 2363 (w), 2104 (m), 1602 (w), 1459 (s), 1438 (s), 1348 (s), 1327 (vs), 1256 (m), 1171 (m), 1129 (s), 1116 (s), 1075 (vs), 1042 (w), 978 (m), 936 (w), 899 (s), 830(s), 755 (m) cm^{-1}. GC−MS (EI, 70 eV) calcd for $C_9H_{13}N$: *m/z* = 135.21. Found: 135 ($M^{\bullet+}$).

Cyclopolymerizations with Ru-Based Initiators. All polymerizations with **I1**−**I4** were performed under a nitrogen atmosphere. A typical procedure was as follows: A solution of initiator **I1** (0.0047 g, $6{\cdot}10^{-6}$ mol) in 0.4 mL of chloroform was added to a solution of **M1** (0.2919 g, $6{\cdot}10^{-4}$ mol) in 0.4 mL of chloroform at 45 °C. The mixture was stirred for 4 h at 45 °C, then 0.8 mL of ethyl vinyl ether was added and the mixture was stirred for extra 30 min at elevated temperature. The solvent was removed *in vacuo*, then 10 mL of methanol were added and the resultant suspension was filtered. The polymer was collected as a dark red powder by filtration and thoroughly washed several times with fresh portions of methanol and then dried *in vacuo* at 45 °C. Isolated yield: 0.098 g (34%).

Poly-M1. ^{1}H NMR (DMSO-d_6): δ = 6.82 (s, 2H, polymer backbone $\mathrm{{=}CH{-}C{=}C{-}}\mathit{CH}\mathrm{{=}}$), 4.77 (s, 4H, cyclic $\mathrm{N{-}}\mathit{CH}_2\mathrm{{-}C{=}}$), 3.53 (s, 4H, $\mathrm{{=}N{-}(}\mathit{CH}_2\mathrm{{-}CH_2{-}CH_2{-}CH_3)_2}$), 1.67 (s, 4H, $\mathrm{{=}N{-}(CH_2{-}}\mathit{CH}_2\mathrm{{-}CH_2{-}CH_3)_2}$), 1.37 (s, 4H, $\mathrm{{=}N{-}(CH_2{-}CH_2{-}}\mathit{CH}_2\mathrm{{-}CH_3)_2}$), 0.95 (s, 6H, $\mathrm{{=}N{-}(CH_2{-}CH_2{-}CH_2{-}}\mathit{CH}_3\mathrm{)_2}$). ^{13}C NMR (DMSO-$d_6$): δ = 13.2 ($\mathrm{{=}N{-}(CH_2{-}CH_2{-}CH_2{-}}\mathit{CH}_3\mathrm{)_2}$), 19.0 ($\mathrm{{=}N{-}(CH_2{-}CH_2{-}}\mathit{CH}_2\mathrm{{-}CH_3)_2}$), 24.7 ($\mathrm{{=}N{-}(CH_2{-}}\mathit{CH}_2\mathrm{{-}CH_2{-}CH_3)_2}$), 63.5 (cyclic $\mathrm{N{-}}\mathit{CH}_2\mathrm{{-}C{=}}$), 67.5 ($\mathrm{{=}N{-}(}\mathit{CH}_2\mathrm{{-}CH_2{-}CH_2{-}CH_3)_2}$), 122.6−116.2 (q, anion, J_{CF} = 321.9 Hz), 122.0 (polymer backbone $\mathrm{{=}CH{-}C{=}}\mathit{C}\mathrm{{-}CH{=}}$), 132.3 (polymer backbone $\mathrm{{=}CH{-}C{=}C{-}}\mathit{CH}\mathrm{{=}}$). IR (ATR mode): 2968 (m), 2879 (m), 1458 (m), 1411 (s), 1346 (s), 1179 (vs), 1132 (vs), 1050 (vs), 955 (s), 891 (m), 790 (s), 738 (s), 651 (vs), 613 (vs) cm^{-1}. M_n = 13 400, M_w = 18300; PDI = 1.37.

Typical Polymerization in Ionic Liquids. I3 (0.0050 g, $6{\cdot}10^{-6}$ mol) was dissolved under a nitrogen atmosphere at 45 °C in 0.3 g of 1,2-dimethyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide, M2 (0.2414 g, $6{\cdot}10^{-4}$ mol) was dissolved in 0.3 g of the same IL at 45 °C. The solution of the initiator was rapidly added to the monomer solution. An immediate change in color from yellow to lilac-magenta was observed. The mixture was stirred for 4 h at 45 °C, then 0.8 mL of ethyl vinyl ether was added and the mixture was stirred for extra 30 min at elevated temperature. Finally, the reaction mixture was poured into a large excess of methanol. The polymer was separated as red-black powder by filtration. After washing with fresh methanol the polymer was dried *in vacuo* at 45 °C. Yield: 0.060 g (30%).

Poly-M2. ^{1}H NMR (DMSO-d_6): δ = 6.86 (s, 2H, polymer backbone $\mathrm{{=}CH{-}C{=}C{-}}\mathit{CH}\mathrm{{=}}$), 4.75 (s, 4H, cyclic $\mathrm{N{-}}\mathit{CH}_2\mathrm{{-}C{=}}$), 3.38 (s, 6H, $\mathrm{{=}N{-}(}\mathit{CH}_3\mathrm{)_2}$). ^{13}C NMR (DMSO-$d_6$): δ = 53.3 ($\mathrm{{=}N{-}(}\mathit{CH}_3\mathrm{)_2}$), 70.5 (cyclic $\mathrm{N{-}}\mathit{CH}_2\mathrm{{-}C{=}}$), 123.2−116.2 (q, anion, J_{CF} = 322.1 Hz), 123.2 (polymer backbone $\mathrm{{=}CH{-}C{=}}\mathit{C}\mathrm{{-}CH{=}}$), 132.7 (polymer backbone $\mathrm{{=}CH{-}C{=}C{-}}\mathit{CH}\mathrm{{=}}$). IR (ATR mode): 3055 (m), 2970 (m), 2927 (w), 2873 (w), 1480 (s), 1456 (w), 1419 (w), 1384 (s), 1352 (vs), 1331 (s), 1191 (vs), 1133 (vs), 1053 (vs), 987 (s), 954 (m), 922 (m), 788 (s), 762 (m), 740 (s), 654 (m), 615 (vs), 600 (s), 570 (vs), 512 (s) cm^{-1}. Raman, $\Delta\nu$: 2787 (w), 2432 (w), 2084 (w), 1553 (vs, $\nu_{\mathrm{C=C}}$), 1519 (vs, $\nu_{\mathrm{C=C}}$), 1436 (w), 1319 (s), 1234 (s), 1206 (vs), 975 (w), 938 (w), 909 (m), 843 (s), 773 (w), 568 (m), 425 (w), 312 (w), 154 (w) cm^{-1}. $M_{\mathrm{n}} = 18600$; $M_{\mathrm{w}} = 20\,400$; PDI = 1.09.

Poly-M3. ^{1}H NMR (DMFA-d_7): $\delta = 7.42$ (s, 2H, polymer backbone $=\mathrm{CH{-}C{=}C}\text{-}\mathit{CH}{=}$), 5.21 (s, 4H, cyclic $\mathrm{N{-}}\mathit{CH_2}\mathrm{{-}C{=}}$), 4.35 (s, 4H, $=\mathrm{N{-}}\mathit{CH_2}\mathrm{{-}CH_2{-}O{-}CH_2{-}}\mathit{CH_2}\text{-}$), 3.79 (s, 4H, $=\mathrm{N{-}CH_2{-}}\mathit{CH_2}\mathrm{{-}O{-}}\mathit{CH_2}\mathrm{{-}CH_2{-}}$). ^{13}C NMR (DMFA-$d_7$): $\delta = 61.2$ ($=\mathrm{N{-}}\mathit{CH_2}\mathrm{{-}CH_2{-}O{-}CH_2{-}}\mathit{CH_2}\text{-}$), 62.2 ($=\mathrm{N{-}CH_2{-}}\mathit{CH_2}\mathrm{{-}O{-}}\mathit{CH_2}\mathrm{{-}CH_2{-}}$), 68.6 (cyclic $\mathrm{N{-}}\mathit{CH_2}\mathrm{{-}C{=}}$), 125.1−115.5 (q, anion, $J_{\mathrm{CF}} = 321.8$ Hz), 123.8 (polymer backbone $=\mathrm{CH{-}}\mathit{C}{=}\mathit{C}\mathrm{{-}CH{=}}$), 132.5 (polymer backbone $=\mathrm{CH{-}C{=}C{-}}\mathit{CH}{=}$). IR (ATR mode): 3057 (w), 3006 (m), 2879 (w), 1467 (m), 1408 (w), 1343 (s), 1321 (s), 1274 (w), 1173 (vs), 1124 (vs), 1047 (vs), 987 (m), 936 (s), 891 (m), 857 (m), 790 (w), 739 (m) 652 (m) cm^{-1}. $M_{\mathrm{n}} = 19400$; $M_{\mathrm{w}} = 20\,800$; PDI = 1.07.

Typical Polymerization Using Schrock Initiators I4 and I5. All polymerizations were performed under glovebox conditions. A solution of **M2** (0.1464 mg, 3.6×10^{-4} mol) in chloroform (2 mL) and a solution of **I5** (0.0028 g, $3.6 \cdot 10^{-6}$ mol) in chloroform (1 mL) were cooled at −37 °C for 20 min. Then the initiator solution was added to the monomer solution under vigorous stirring. After 4 h at room temperature, an excess of ferrocene carbaldehyde (6 mg) was added, and the violet reaction mixture was stirred for 1 h. The mixture was poured on the filter and the polymer was washed several times with chloroform. The product was taken out of the glovebox and dried in vacuum at 45 °C to yield deep red to black powder. Yield: 0.1438 g (98%). According to ^{1}H NMR, the polymer consisted of ca. 70% 5-membered and ca. 30% 6-membered cyclic units. Raman, $\Delta\nu$: 2756 (w), 2422 (w), 1548 (vs, $\nu_{\mathrm{C=C}}$), 1517 (vs, $\nu_{\mathrm{C=C}}$), 1429 (m), 1391 (w), 1358 (w), 1311 (s), 1206 (vs), 958 (m), 929 (m), 840 (s), 774 (w), 558 (m), 309 (w), 153 (w), 28 (w) cm^{-1}. $M_{\mathrm{n}} = 20\,500$; $M_{\mathrm{w}} = 21\,400$; PDI = 1.05.

Conclusions

A series of ruthenium- and molybdenum-based metathesis catalysts have been investigated for their capability of polymerizing polar, nonionic and ionic 1,6-heptadiynes based on amines, various quaternized ammonium salts and the bis(trifluoromethylsulfonyl)imide anion. The most relevant findings were that (i) ruthenium bistrifluoroacetate derived catalysts were capable of polymerizing these monomers in a regioselective manner thus forming one single repeat unit; however, in low yields and with low molecular weights; (ii) molybdenum hexafluoro-*tert*-butoxide-based initiators polymerize these monomers in virtually quantitative yields, however, in a non-regioselective manner, thus forming two types of repeat units; (iii) the ILs used have demonstrated some advantages as solvents for the polymerization of monomers that are insoluble in common organic solvents. Finally, the bis(trifluoromethylsulfonyl)imide polyenes prepared here possess the highest ionic conductivity among the polymeric analogs of the same type and show some intriguing properties such as solvatochromic behavior.

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