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PEG-Bis Phosphonic Acid Based Ionic Supramolecular Structures

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Summary: A number of supramolecular structures are prepared by mixing stoichiometric amounts of a phosphonic acid terminated poly(ethylene glycol) with propargyl amine, hexamethylene diamine, tris(2-aminoethyl)amine, and the first generation of a poly(propylene imine) dendrimer in turn at room temperature. The resulting ionic assemblies are very comprehensively characterized by ATR-FTIR, proton, and carbon-13 NMR spectroscopy that unequivocally demonstrate the ionic network formation through ammonium phophonates. The resulting salt and ionic networks are additionally analyzed by differential scanning calorimetry and thermogravimetric analysis. The conclusion is that mixing the virgin components at room temperature spontaneously form either a salt or ionic supramolecular networks.

Keywords: differential scanning calorimetry; ionic networks; IR spectroscopy; NMR spectroscopy; supramolecular chemistry; thermogravimetric analysis

Introduction

The supramolecular chemistry have exploited the non-covalent interactions such as hydrogen bonds, electrostatic ionic bonds, $\pi - \pi$ stacking, metal-ligand bonds, or hydrophobic interactions for decades.[1] Often low molar mass building blocks or monomers are exploited to create supramolecular polymers which additionally display a reversible feature that can improve processing, induce self-healing behavior or provide stimuli responsiveness. The ionic interactions in particular offer a great potential in this respect due to the immense arsenal of available starting materials. In this respect the emergence of building blocks from renewable sources is important. Also the introduction of the new cations and anions emerging from the ionic liquid (IL) chemistry community has revitalized classical applications of polyelectrolytes,[2] to related fields like energy conversions,[3] gas separation membranes[4] or stimuli-responsive materials.[5] Moreover many of the self-assembling properties of ILs have been utilized in the classical polymer fields. Of particular interest is the pioneering work by Wathier and Grinstaff[6] reporting on preparation of supramolecular ionic networks based on multicationic and multianionic building blocks, however, employing somehow complex ILs. More recently Mecerreyes and coworkers presented supramolecular ionic polymers based on small di- or trifunctional carboxylic acids that were allowed to form ammonium carboxylates by reaction with di- or trialkyl amines.[7] These materials combine the unique rheological properties related to supramolecular polymers where a sharp transition between a viscoelastic gel and a viscous liquid provides an unique relationship between the ionic conductivity and the temperature. It was furthermore argued that the chemistry sets the scene for preparation of polymer materials with self-healing properties. Additionally the same group[8] synthesized supramolecular ionic networks based on citric acid and aliphatic diamines. Here it was demonstrated that the dynamic viscoelastic behavior of the

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supramolecular networks were the same in both solid and liquid states. We recently introduced the preparation of supramolecular polymeric networks by simple room temperature mixing of neat carboxylic acid terminated poly(ethylene glycol) PEG of various lengths and first or second generation of multifunctional dendritic amines of poly(propylene imine).[9] The resulting supramolecular ionic networks displayed a significantly higher thermal stability than the constituting precursors.

Here we introduce a new family of polymeric ionic networks where the core molecule is phosphonic acid terminated PEG (of molecular weight ~840) that is reacted with various amines with primary amine functionality from 2–4. This generic type of ionic networks where the cross-linking units are various ammonium ions are of particular interest for potential applications in interpenetrating networks to be used as dielectric electroactive polymers in actuator applications. The ionic networks are expected to attain high dielectric permittivity especially at the desired low frequencies employed in wave energy harvesting.

Experimental Part

Materials

Bis Propylphosphonic acid-PEG 840 ($DiPO(OH)_2$-PEG 840) (Specific Polymers, Clapiers, France), first generation poly (propylene imine) dendrimer based on a diaminobutane core (PPI G1) (SyMO-Chem BV, Eindhoven, The Netherlands), hexamethylene diamine (HMDA) (Aldrich), tris(2-aminoethyl)amine (TAEA) (Aldrich), and propargyl amine (PPGA) (Aldrich) were used as received.

Sample Preparation

The supramolecular structures were all prepared by brief stirring of the stoichiometric amounts of the components at room temperature. Five minutes stirring in all instances transformed the liquid starting materials into solids.

Characterization

The attenuated total reflectance (ATR) FTIR analysis was performed on Perkin-Elmer Spectrum One. The spectra were recorded in the range of 4000–600 cm^{-1} with 4 cm^{-1} resolution. NMR spectra were recorded on a Bruker 300 MHz instrument employing D_2O as solvent at 25 °C. The thermal transitions (glass transition temperatures (T_g) and melting points (T_m)) were determined with a DSC Q1000 calorimeter from TA instruments with heating and cooling rates of 20 °C min^{-1} on 9–12 mg samples. T_g was determined from the second heating trace as the midpoint of the transition. Thermal stability was assessed by thermogravimetric analysis (TGA) by use of a TGA Q500 TA instrument ranging from 20 to 600 °C at a heating rate of 20 °C min^{-1} under nitrogen.

Results and Discussion

The supramolecular structures were generated by mixing Bis Propylphosphonic acid-PEG 840 ($DiPO(OH)_2$-PEG) with various amines of increasing primary amine functionality (f_a): hexamethylenediamine (HMDA) (2), tris(2-aminoethyl)amine (TAEA) (3), and the first generation dendrimer PPI G1 (4) at room temperature. Since the $DiPO(OH)_2$-PEG has difunctional end groups the functionality of the proton donor (f_d) is 4. The network is expected to be linked by ammonium phosphonate pairs. Thus 3-dimensional structures are expected even when the primary amine functionality matches the proton donor functionality. In order to verify the network formation and the claimed structural components a thorough spectroscopic analysis was undertaken by application of ATR-FTIR as well as ^1H and ^{13}C NMR. In fact, also a mono functional amine, propargyl amine (PPGA), was protonated by the proton donor that results in the most simple protonated structure.

Spectroscopic characterization

The chemical structure of the components used and formed in the simple salt formation when $DiPO(OH)_2$-PEG 840 protonates

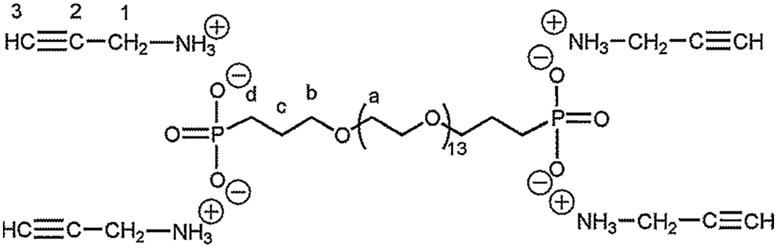

Figure 1.
Structure of DiPO$(OH)_2$-PEG 840: PPGA salt (**1**).

propargyl amine (PPGA) in a 1:4 molar ratio is shown in Figure 1 (the numbers and small letters are employed in Tables 1 and 2).

Figure 2 depicts the FTIR spectra of all components involved in this salt formation. Inspection of the spectrum of the pure DiPO$(OH)_2$-PEG reveals the wide absorption band at 3600–3200 cm^{-1}, with a maximum at about 3403 cm^{-1} that can be assigned to the O-H stretching mode of hydroxyl groups and adsorbed water. The band at 1662 cm^{-1} could be attributed to H-O-H deformation of adsorbed water[10] and the absorption peak at 1246 cm^{-1} can be ascribed to P=O deformation vibration.[11] Durmus *et al.*[12] assigned a band at 1143 cm^{-1} to the stretching mode (P = O) for a poly(vinyl phosphonic acid) sample. Additionally, absorbances at 2340, 985, and 936 cm^{-1} belong to (=O)PO-H vibration.[13–18] Indeed, all these peaks are not present in the spectrum of the DiPO$(OH)_2$-PEG/PPGA salt. These bands have been replaced by several new bands at 1624, 1557, 1217, 1023, and 913 cm^{-1}. Furthermore, in the salt spectrum, the band at 3365 cm^{-1} related to the N-H stretching vibrations of the PPGA amino group is suppressed. New bands at 3242, 2867, 2663 and 2125 cm^{-1} have appeared. The sharp peak at 2867 cm^{-1} is attributed to both the C-H stretching vibrations from the alkyne group and the CH_2 stretching vibrations of the alkane moiety. The latter have shifted from 2923 and 2853 cm^{-1} in the pure

Table 1.
Proton chemical shifts (ppm in D_2O (multiplicity)) of DiPO$(OH)_2$-PEG 840, multifunctional amines, and the supramolecular ionic structures derived.

Chemical structure	Protons								
	1	2	3	4	5	a	b	c	d
a b c d $-(CH_2CH_2O)_nCH_2CH_2CH_2\text{-}PO_2H_2{}^*$						3.55(s)	3.45(t)	1.68(s)	1.71(s)
3 1 $HC{\equiv}CCH_2NH_2$(PPGA)	4.71(s)		3.30(s)						
Ionic salt (1)	4.67(s)		3.62(s)			3.55(s)	3.42(t)	1.34(m)	1.61(m)
3 2 1 $-(CH_2CH_2CH_2NH_2)_2$ (HMDA)	2.54(t)	1.36(t)	1.26(m)						
Ionic network (2)	2.83(t)	1.53(m)	1.27(m)			3.55(s)	3.41(t)	1.27(m)	1.53(m)
2 1 $N(CH_2CH_2NH_2)_3$ (TAEA)	2.67(t)	2.50(t)							
Ionic network (3)	2.97(t)	2.66(t)				3.55(s)	3.40(t)	1.24(m)	1.57(m)
1 2 3 4 5 $-(CH_2CH_2N(CH_2CH_2CH_2NH_2)_2)_2$ (PPI G1)	1.34(m)	2.37(m)	2.37m)	1.50(m)	2.50(t)				
Ionic network (4)	1.60(m)	2.53(m)	2.53(m)	1.74(m)	2.85(t)	3.55(s)	3.40(t)	1.25(m)	1.37(m)

* phosphonic acid protons resonate at 4.73 ppm.

Table 2.
Carbon-13 chemical shifts (ppm in D_2O) of DiPO(OH)$_2$-PEG 840, multifunctional amines, and the supramolecular ionic structures derived.

Chemical structure	Carbons								
	1	2	3	4	5	a	b	c	d
a b c d									
-$(CH_2CH_2O)nCH_2CH_2CH_2\text{-}PO_3H_2$						69.6	69.1	22.1	23.8
3 2 1									
$HC{\equiv}CCH_2NH_2$(PPGA)	29.7	84.2	71.6						
Ionic salt (1)	29.0	75.5	71.7			69.6	69.0	23.5	24.0
3 2 1									
-$(CH_2CH_2CH_2NH_2)_2$(HMDA)	40.6	31.9	26.1						
Ionic network (2)	39.2	26.5	25.1			69.5	69.0	23.9	24.4
2 1									
$N(CH_2CH_2NH_2)_3$ (TAEA)	37.9	56.4							
Ionic network (3)	36.9	50.9				69.5	69.1	24.1	24.6
1 2 3 4 5									
-$(CH_2CH_2N(CH_2CH_2CH_2NH_2)_2)_2$ (PPI G1)	23.5	53.0	50.8	28.4	39.2				
Ionic network (4)	22.9	52.7	50.0	23.3	37.7	69.5	69.0	24.1	24.6

PPGA. Additionally, the characteristic shoulder at $\sim$2663 cm^{-1} associated with the -NH_3^+ absorption band is identified. The band at $\sim$2125 cm^{-1} is ascribed to the $C{\equiv}C$ stretching absorption of the alkyne groups. All these observations strongly support complete protonation of all amino groups originally present in the mixture.

The salt formation was additionally analyzed by NMR spectroscopy in D_2O. Figure 3 shows the proton NMR spectra of the starting components and the salt (**1**). The chemical shifts and the resonance multiplicity are listed in Table 1. The proton spectrum of PPGA (Figure 3.2) is verysimple consisting of only 2 singlets where the area of **1** is twice

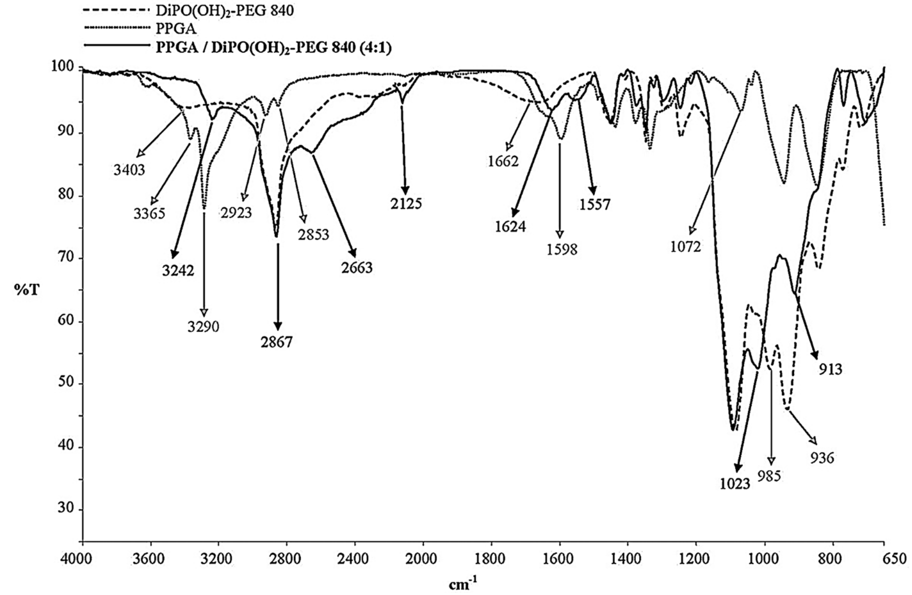

Figure 2.
ATR-FTIR spectra of DiPO(OH)$_2$-PEG 840, PPGA, and the salt (1) formed from a PPGA/DIPO(OH)$_2$-PEG 840 (4:1) mixture.

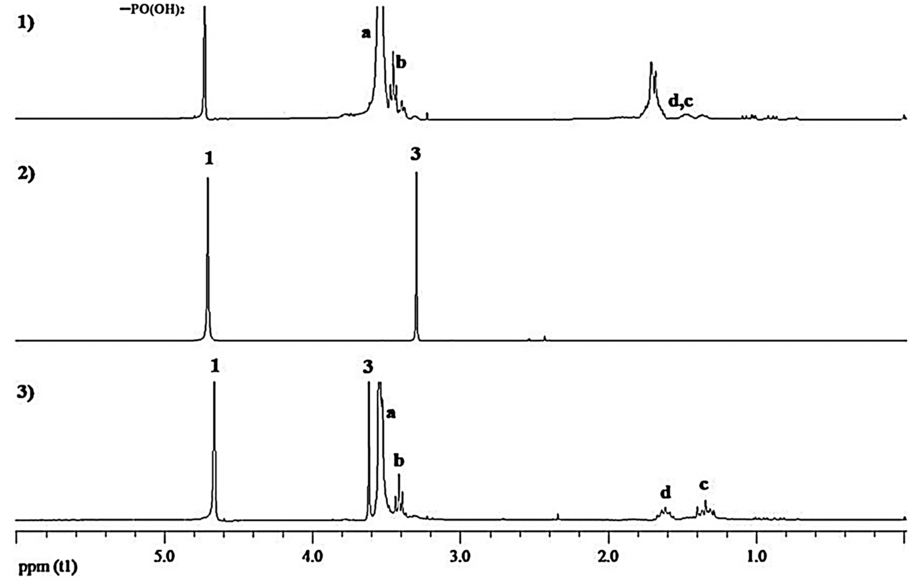

Figure 3.
Proton NMR of DiPO(OH)$_2$-PEG 840 (1), PPGA (2) and the salt 1 (3).

that of **3**. The singlets are clearly visible in the salt spectrum (Figure 3.3) where the methylenes (1) next to the ammonium ion have experienced a 0.32 ppm deshielding. Most importantly is the complete lack of any PPGA in the salt spectrum strongly supporting the total salt formation between the stoichiometric reactants. Also the complete disappearance of the phosponic acid protons at 4.73 ppm is noticed. In the centre part of the DiPO(OH)$_2$-PEG 840 salt the largest effect is noticed for the c methylenes that are shielded almost 0.34 ppm. Similar pronounced effects are observed in the carbon-13 NMR spectra of the salt components shown in Figure 4 with the carbon-13

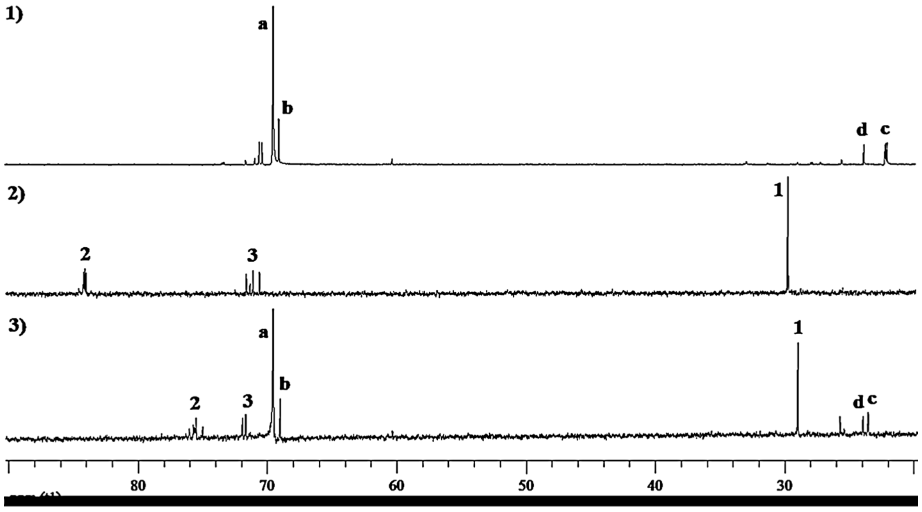

Figure 4.
Carbon-13 NMR spectra of DiPO(OH)$_2$-PEG 840 (1), PPGA (2), and salt **1** (3).

chemical shifts listed in Table 2. A large 8.7 ppm shielding is experienced for the quaternary 2 carbon, whereas methylene carbon 1 feels a ~1 ppm deshielding in the salt. The rather large differences in the shielding observed is due to the inherent nature of the neighbour effects caused by ammonium ions as compared to the amines.

In summary, the three spectroscopic techniques all unequivocally point to the supramolecular salt formation.

Figure 5 illustrates the ammonium phosphonates that link the components of the ionic network 2 formed from the 2 hexamethylenediamine (HMDA):1 DiPO-$(OH)_2$-PEG 840 mixture.

The ionic supramolecular structure of this ionic network was also analyzed by infrared spectroscopy where especially in the network **2** spectrum the stretching vibrations of -NH_2 asymmetric and symmetric bands of HMDA ranging from 3329 to 3170 cm^{-1} are suppressed as compared to the situation in the HMDA spectrum. Additionally, the protonation of the -NH_2 groups of HMDA is strongly suggested by the disappearance of the band at 1606 cm^{-1} attributed to the strong in-plane -NH_2 scissoring bending vibration of the non-protonated HMDA. Furthermore, the characteristic shoulders at ~2653, 2572 and ~2245 cm^{-1} corresponding to the -NH_3^+ absorption bands are clearly visible in the spectrum of the ionic network **2**.

The proton chemical shifts of the ionic network **2** are listed in Table 1. In the network both methylene protons in α-position (1) and in β-position (2) to the ammonium ions are deshielded as compared to the resonances in the HMDA. Thus the 1 methylenes are deshielded by 0.3 ppm and the 2 methylenes a little less by 0.17 ppm. Similarly the carbon-13 resonances listed in Table 2 clearly show significant differences between the HMDA and the ionic network **2**. The resonances of carbons 1, 2, and 3 in the network are all shielded although to different degrees with 2 experiencing a large (5.4 ppm) difference as also observed previously in the similar salt spectrum. In summary the spectroscopies conclusively corroborate the ionic network formation.

Figure 6 illustrates the cross-linking units of the ionic network **3** based on TAEA and DiPO$(OH)_2$-PEG 840 in a 1: 0.75 molar ratio.

In the ionic network FTIR spectrum the asymmetric and symmetric stretching vibration bands of -NH_2 of TAEA at 3357 and 3276 cm^{-1} are completely suppressed. Also the strong in-plane -NH_2 scissoring bending vibration of the non-protonated TAEA at 1590 cm^{-1} is absent in the spectrum of the ionic network **3**. Additionally, the characteristic shoulders at about 2628, 2532 and 2238 cm^{-1} associated with the -NH_3^+ absorption bands are identified in the spectrum of **3** substantiating the protonation of the primary amino groups of TAEA. Moreover, another strong indication of the protonation of the primary amino groups of TAEA, is the disappearance of the broad band around 861 cm^{-1} associated with the out-of-plane wagging (bending vibrations) of -NH_2, which is characteristic

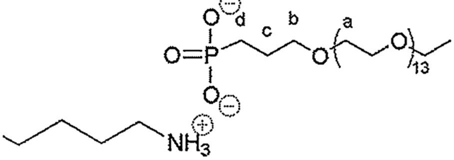

Figure 5.
Ionic components in ionic network 2.

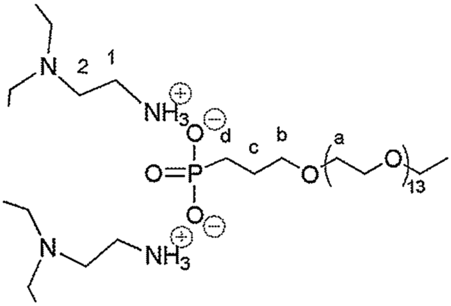

Figure 6.
Basic ionic components in ionic network 3.

of primary amines. Similar results were observed in a previous work when TAEA was employed in a similar fashion to create ionic networks with two short biscarboxymethyl ether terminated poly(ethylene glycols) (DiCOOH-PEGs).[9] In addition the new bands at 1628, 1556, 1213, 974 and 767 cm^{-1} confirm the protonation of the amino groups of TAEA. The bands at 985 and 936 cm^{-1} ascribed to (O=)PO-H vibration in the DiPO(OH)$_2$-PEG 840 spectrum, are not present in the spectrum of the ionic network **3**.

The proton NMR spectrum of TAEA is also very simple with only two coupled triplets with the shifts listed in Table 1. In the ionic network **3** both triplets are significantly deshielded with the largest effect (0.3 ppm) on methylene protons 1. In case of the methylenes 2 the difference is 0.16 ppm. Neither of the original resonances from the TAEA spectrum are visible in the ionic network spectrum. However, the short ethylene chains between the primary amines and the tertiary amine in TAEA prevent NMR to provide information on possible protonation of the tertiary amine in the ionic network. Similar observations are made in the carbon-13 spectra with the chemical shifts listed in Table 2. Here the carbon 2 in the network **3** spectrum is shielded 5.5 ppm compared to the TAEA spectrum, whereas a smaller difference (1 ppm) is observed for carbon 1. Again the results of the NMR analyses very strongly support the findings from FTIR that all primary amines of TAEA take part in the ionic network **3** formation.

The mixing of stoichiometric amounts of DiPO(OH)$_2$-PEG 840 and PPI G1 created the ionic network **4**. The cross-linking unit of the ionic network **4** involving 4 ammonium phosphates from one PPI G1 is shown in Figure 7.

The structure of the ionic network 4 was elucidated by use of the overlaid FTIR spectra displayed in Figure 8. Most of the features already discussed for the salt (1) and the other ionic networks (2 and 3) can be identified in the spectrum of this ionic network as well. An important observation is the lack of the NH$_2$ asymmetric and symmetric bands from PPI G1 dendrimer at 3355 and 3277 cm^{-1} in the network spectrum implying complete protonation of the external primary amino groups of the dendrimer. Also the bending NH$_2$ band of the non-protonated starting dendrimer at 1596 cm^{-1} is not present in the network spectrum. Another interesting observation is the symmetric stretching band of the CH$_2$ groups attached to the tertiary nitrogen

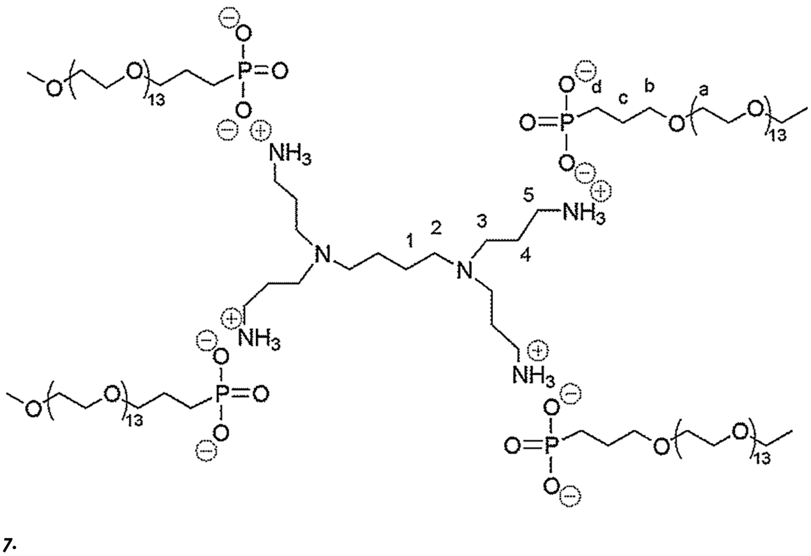

Figure 7.
Ionic components in ionic network 4.

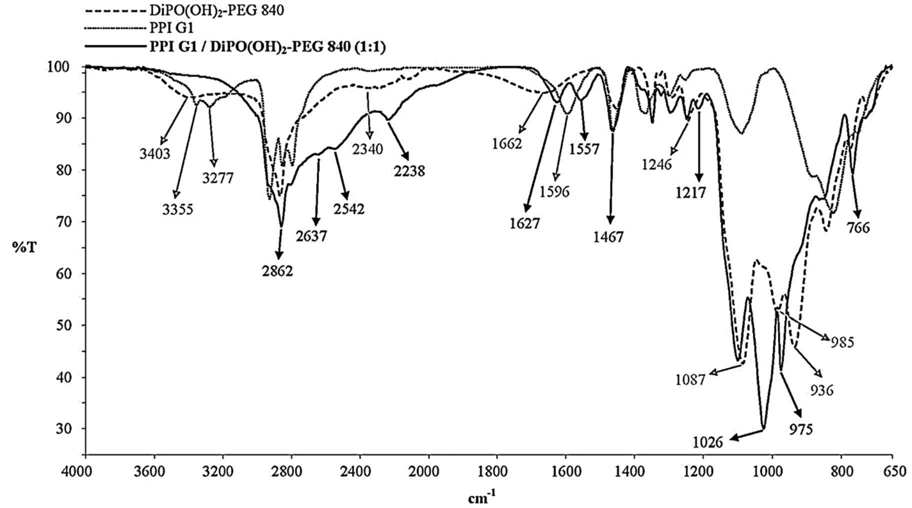

Figure 8.
ATR-FTIR spectra of DiPO$(OH)_2$-PEG 840, PPI G1, and the ionic network (4) formed from a PPI G1/DiPO$(OH)_2$-PEG 840 (1:1) mixture.

located at 2862 cm^{-1}, which is seen in both the dendrimer and (unaltered) in the ionic network spectra, and thus implying no protonation of the tertiary amines. This band should normally be detected at 2850 cm^{-1} and it would be related to the interactions between the lone pair of the nitrogen and the C-H bond, which lies in a *trans* position to it.[19,20] This effect does not occur when the lone pair is delocalized or donated into a vacant orbital. The ionic network spectrum similarly lacks the two strong absorptions at 985 and 936 cm^{-1} associated with the (O =)PO-H absorption identified in the DiPO$(OH)_2$-PEG 840 spectrum. Taken together all these observations seem to confirm the protonation of the external primary amino groups only and the ionic network 4 cross-linked by the unit displayed in Figure 7.

The structural elucidation of the ionic network 4 was supplemented by analyses of the proton NMR spectra displayed in Figure 9 and the carbon-13 spectra shown in Figure 10 with the corresponding chemical shifts collected in Tables 1 and 2. In the proton spectrum of PPI G1 in D_2O (Figure 9.1) the resonances of methylenes 1, 4 and 5 are well separated, where as methylenes 2 and 3 surrounding the tertiary N are overlapped. In the ionic network spectrum (Figure 9.2) the 5 methylene α to

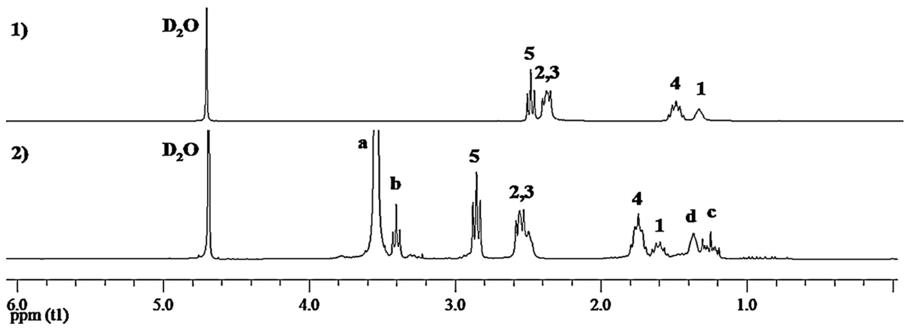

Figure 9.
Proton NMR spectra PPI G1 (1), and network 4 (2).

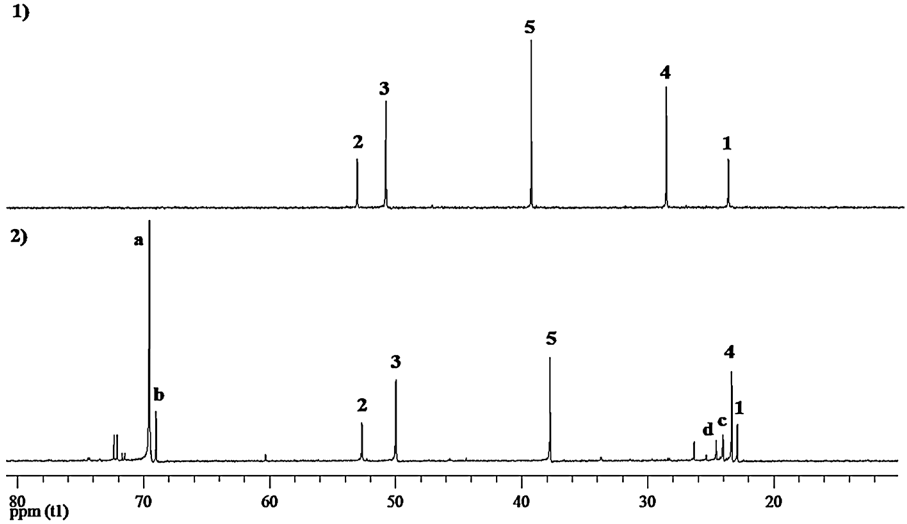

Figure 10.
Carbon-13 NMR spectra of PPI G1 (1), and network 4 (2).

the ammonium ions is deshielded by 0.35 ppm to a position at 2.85 ppm. Also the methylenes 4 in β position to the ammonium ions are deshielded from 1.50 to 1.74 ppm. On the other hand, the d protons next to the phosphonic acid groups are shielded in ionic network to 1.37 ppm from originally 1.71 ppm in the unreacted phosphonic acid.

The carbon-13 spectrum of unreacted PPI G1 (Figure 10.1) shows the resonances of the 5 different methylene carbons. These resonances are also clearly identified in the ionic network spectrum (Figure 10.2) where the most noticeable effects are the shieldings of the 2 methylene carbons closest to the ammonium ions where 5 has moved from 39.2 ppm to 37.7 ppm and 4 from 28.4 ppm to 23.3 ppm. The remaining carbons (1,2,3) in the core of PPI G1 or closest to the tertiary N are almost unaffected in the ionic network spectrum. In addition some deshielding effects are noticed on the d and c methylenes of the phosphonate part of the ionic network.

In summary, the performed NMR analyses support the conclusions of the FTIR analysis that only the primary amines are involved in the formation of the ionic network and thus strongly corroborate the cross-linking unit of ionic network 4 displayed in Figure 7. It is noted that both ^{31}P and ^{15}N NMR spectroscopy although not performed could further strengthen the spectroscopical conclusions where the former would monitor the behaviour of the PEG chain ends, and the latter additionally probe the amine behaviour within the networks.

Thermal Investigations

The thermal transitions of the phosphonic acid based supramolecular ionic structures were analyzed by DSC. The results are listed in Table 3 and, for the sake of comparison, results of similar investigations on ionic structures based on a biscarboxylic acid terminated PEG were also included. The phosphonic acid based ionic networks clearly reveal a more complex behaviour with two T_gs, of which the lowest one is quite close to the T_g of the precursor DiPO(OH)$_2$-PEG 840. This T_g is thus tentatively assigned to the longer PEG chains of these networks. The fact that two T_g's appear in each network suggests some kind of phase separation within the network. The longer PEG chain in DiPO-(OH)$_2$-PEG 840 is apparently a decisive factor. The higher T_g is hypothesized to be due to ion clusters that are formed at each end of the phosphonic acid precursors or

Table 3.
Transition temperatures of supramolecular ionic networks based on PEGs terminated with carboxylic acids and phosphonic acids and of the precursors.

Entry	Chemical structure	(molar ratio)	T_{g1} (°C)	T_{g2} (°C)	T_m (°C)	Ref.
1	PPI G1		−107			9
2	DiCOOH-PEG 600		−60			9
3	$DiPO(OH)_2$-PEG 840		−46			this work
4	HMDA:DiCOOH-PEG 600	1:1	−30			9
5	HMDA:$DiPO(OH)_2$-PEG 840	2:1	−49	−3	138	this work
6	TAEA:DiCOOH-PEG 600	1:1.5	−24			9
7	TAEA:$DiPO(OH)_2$-PEG 840	2:1.5	−40	5		this work
8	PPI G1:DiCOOH-PEG 600	1:2	−25			9
9	PPI G1:$DiPO(OH)_2$-PEG 840	1:1	−45	26		this work

around the multifunctional amines. These clusters apparently has less local mobility than the PEG segments. In fact the largest cluster that is anticipated formed with the PPI G1 dendrimer is expected to have the lowest mobility. The highest T_g (26 °C) is also observed here. In the case of the HMDA/$DiPO(OH)_2$-PEG 840 (entry 5) even a melting point is additionally identified. A hypothetical explanation is that a poly(phosphonamide) is formed during the heating in the DSC instrument during the analysis. Support for this hypothesis is that polyamides have previously been produced by heating a stoichiometric mixture of HMDA and DiCOOH-PEG 600 at 275 °C. Here there covered polyamide was clearly identified by two new bands at 1660 cm^{-1} (the amide I band) and at 1537 cm^{-1}(the amide II band), associated with the amide linkage. A brief account of this can be found in ref.[9]

The thermal stability of the supramolecular ionic networks and the precursors were

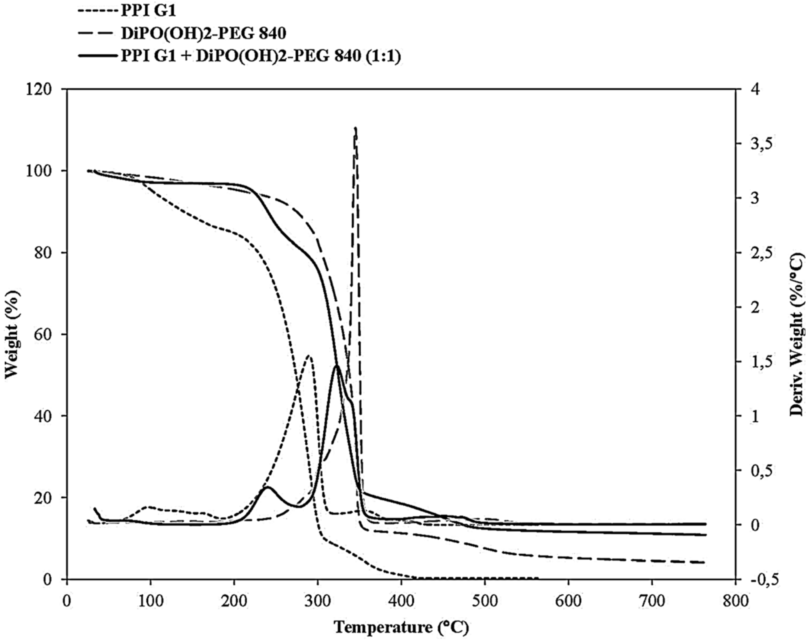

Figure 11.
TGA traces of PPI G1, $DiPO(OH)_2$-PEG 840, and PPI G1:$DiPO(OH)_2$-PEG 840 (1:1) ionic network during heating at 20 °C/min under N_2. Both the weight loss (←)and the first derivative weight loss (→) are shown.

Table 4.
Thermal stability of precursors and supramolecular ionic networks based on PEGs terminated with carboxylic acids and phosphonic acids.

Entry	Formulation/chemical	$T_{d2\%}$[a]	$T_{d10\%}$[a]	T_{max}[b]	Char	Ref
		(°C)	(°C)	(°C)	Yield[c] (%)	
1	HMDA	39	84	127	0.2	this work
2	TAEA	74	116	182	0.3	this work
3	PPI G1	81	139	290	0.3	this work
4	DiCOOH-PEG 600	239	362	414	1.7	9
5	DiPO(OH)$_2$-PEG 840	116	274	345	5.2	this work
6	HMDA:DiCOOH-PEG 600 (1:1)	64	195	420	3.3	9
7	HMDA:DiPO(OH)$_2$-PEG 840 (2:1)	106	247	329	13.1	this work
8	TAEA:DiCOOH-PEG 600 (1:1.5)	140	363	413	4.6	9
9	TAEA:DiPO(OH)$_2$-PEG 840 (2:1.5)	147	264	336	14.4	this work
10	PPI G1:DiCOOH-PEG 600 (1:2)	194	337	411	3.1	9
11	PPI G1:DiPO(OH)$_2$-PEG 840 (1:1)	68	240	322	11.6	this work

[a] Temperature of 2 and 10 wt% loss determined by TGA. [b] Temperature for maximum degradation rate. [c] Char yield at 600 °C.

likewise studied by TGA under nitrogen. Figure 11 shows the analyses of the ionic network PPI G1:DiPO(OH)$_2$-PEG 840 system as a representative example. In order to qualitatively compare the behaviour of the different ionic networks some key numbers are extracted and listed in Table 4 that furthermore contains similar information from the carboxylic acid based PEG networks. A striking feature is the much lower thermal stability of phosphonic acid containing PEG (Table 4 entry 5) compared to the carboxylic acid based analogue (entry 4) where the difference for the 10% weight loss ($T_{d10\%}$) is 88 °C. This cannot be due to the PEG chains since these are quite comparable in length. Thus the phosphonic acid end groups play a

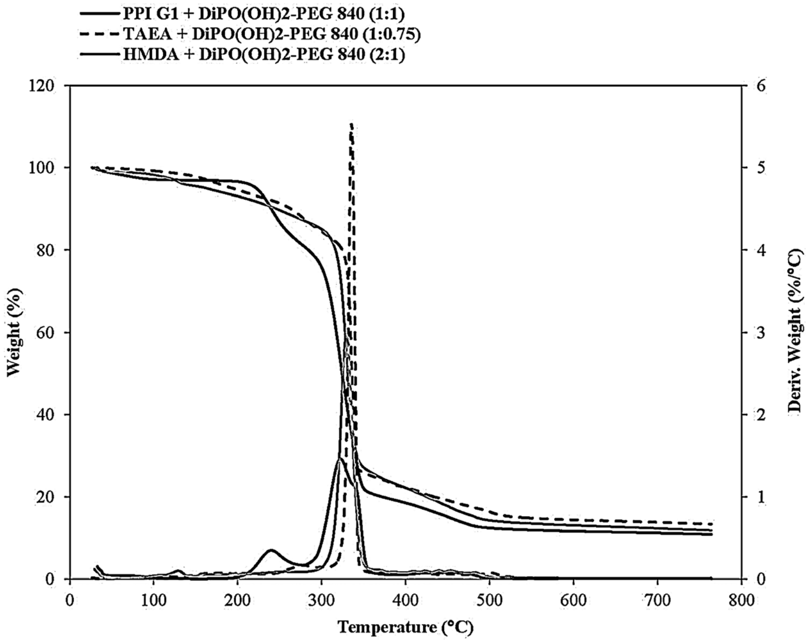

Figure 12.
TGA traces of ionic networks based on DiPO(OH)$_2$-PEG 840, and PPI G1, TAEA, or HMDA during heating at 20 °C/min under N$_2$. Both the weight loss (←) and thefirst derivative weight loss (→) are shown.

deciding role in the degradation process. In general this effect is carried over to the phosphonic acid containing PEG ionic networks since they are all less thermally stable ($T_{d10\%}$ ~50–100 °C lower) than the corresponding carboxylic acid based networks. It is clearly illustrated by Figure 12 that the thermal stability of the phosphonic acid containing networks (entries 7,9,11) is strongly coupled to the stability of the phosphonic acid terminated PEG precursor (entry 5). It is also noted that all the phosphonic acid containing networks have a relatively high char (residue) content (12–14 wt%) at 600 °C, whereas the carboxylic acid based ionic networks only have a 3–5 wt% residue. This may tentatively be attributed to the cleavage of the C-P bond leaving a $PO(OH)_2$ radical that by hydrogen abstraction leads to the formation of phosphorous acid (H_3PO_3). Then this can dehydrate to the oxide, P_2O_3, and water,[21] which can account for the observed residue. In fact, the observed char residue is highest for the TAEA:DiPO$(OH)_2$-PEG 840 network with the highest initial content of phosphonic acid terminated PEG precursor, and lowest for the PPI G1:DiPO$(OH)_2$-PEG 840 network with the lowest PEG precursor content.

Conclusion

The simple mixing of a phosphonic acid terminated PEG with hexamethylene (HMDA), tris-(2-aminoethyl)amine (TAEA), or the first generation PPI dendrimer (PPI G1) has created a new family of supramolecular ionic networks. The spontaneous protonation of the constituting primary amines forming the linking ammonium phosphonates is corroborated by FTIR, proton, and carbon-13 NMR spectroscopy. The ionic networks based on phosphonic acid terminated PEG have higher T_gs than the PEG precursor.In terms of thermal stability, the corresponding carboxylic acid based networks have better stability than the phosphonic acid terminated PEG. The elucidated ionic network strategy suggests the development of novel polymer materials with self-healing properties. Moreover, in combination with orthogonal cross-linking chemistry the design of interpenetrating networks[22] seems an attractive feasible approach.

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