Macromolecular Chemistry and Physics
www.mcp-journal.de

Examining the Properties of (Co)Polymer Networks Prepared by the Phosphane-Ene Reaction

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Polymer networks have emerged as materials with widespread application, including their use in drug delivery, catalysis, and flexible electronics. They have traditionally been derived from organic building blocks using well-developed reaction types. Advances in main group synthetic chemistry have opened the door for the production of new polymer networks, including those containing phosphorus atoms that offer the traits of Lewis basic phosphorus centers. Here, the radical-catalyzed phosphane-ene reaction is used to prepare (co)polymer networks from *i*BuPH$_2$, trivinyltriptycene (TVT), and 1,3,5-triallyl-1,3,5-triazine-2,4,6-trione (TTT), which are the first of their type to include TVT. Networks rich in TVT exhibited greater thermal stability and reduced network mobility compared to those rich in TTT. Despite the rigidity, 3D, and internal free volume associated with the triptycene units present in TVT-rich networks, their swellability is similar to networks rich in TTT indicating that the presence of phosphines may be a dominating factor in the respective structure-property relationships.

1. Introduction

Historically, polymers have generally been considered as 2D chains of one of more repeating unit types. However, just as the complexity of the reaction types and repeating units incorporated into traditional polymers has evolved, so has the study of 2D and 3D polymer networks. These networks are often multicomponent systems that contain a high degree of crosslinking that prevents their dissolution and promotes swelling.[1–7] Hydrophilic examples, known as hydrogels, have found applications, for example, as adhesives,[8,9] drug delivery agents,[10–12] and in flexible electronics.[13]

The majority of examples described above are derived from purely organic building blocks. The chemistry of phosphorus has been exploited more recently to create unique 2D polymers[14–19] that have shown utility in lithium-ion batteries,[20] anion-exchange membranes,[21,22] and as precursors to metal-containing nanomaterials.[23–25] The reactivity of phosphorus-containing molecules has also been exploited in the synthesis of polymer networks.[26–32] One very promising reaction used for network formation is the phosphane-ene (*aka* hydrophosphination) reaction that involves the addition of a P-H bond to an alkene.[33–35] Networks derived from this reaction have been reported to act as self-healing[36] and flame-retardant materials,[37] platforms for the creation of inorganic nanomaterials,[2,38–40] and support or scavenge for catalysts.[41–43] Despite these advances, strategies to alter the porosity and/or swellability of networks prepared via the phosphane-ene reaction remain unexplored.

We address this knowledge gap by preparing (co)polymer networks from *i*BuPH$_2$, 1,3,5-triallyl-1,3,5-triazine-2,4,6-trione (**TTT**), and trivinyltriptycene (**TVT**). *i*BuPH$_2$ was chosen as a relatively inexpensive phosphine that offers two PH bonds necessary for network formation. **TTT** is a relatively flat molecular scaffold bearing three vinyl groups and **TVT** similarly contains three vinyl groups, but also introduces structural rigidity, 3D character, and high internal free volume on account of its triptycene core, which has been widely exploited for the generation of porous network materials.[44–49] The networks reported contain varying quantities of **TTT** and **TVT** and were subjected to both thermal analyses and swellability studies in an attempt to establish structure-property relationships for this family of polymer networks.

2. Results and Discussion

*i*BuPH$_2$ and **TTT** are commercially available, while **TVT** is not. To synthesize **TVT**, we first produced triformyltriptycene (**TFT**) via a modified literature procedure involving the treatment of tripytycene with excess 1,1-dichlorodimethyl ether and TiCl$_4$. In our hands, the yields of this reaction were consistently higher than analogous reactions employing AlCl$_3$ instead of TiCl$_4$ (**Scheme 1**, Table S1, Supporting Information).[50] By comparison with published NMR chemical shifts, the presence of four

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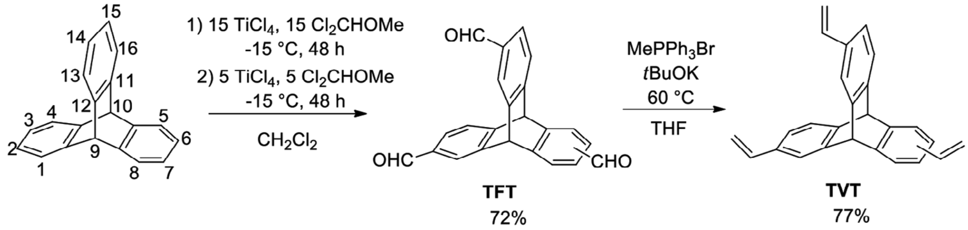
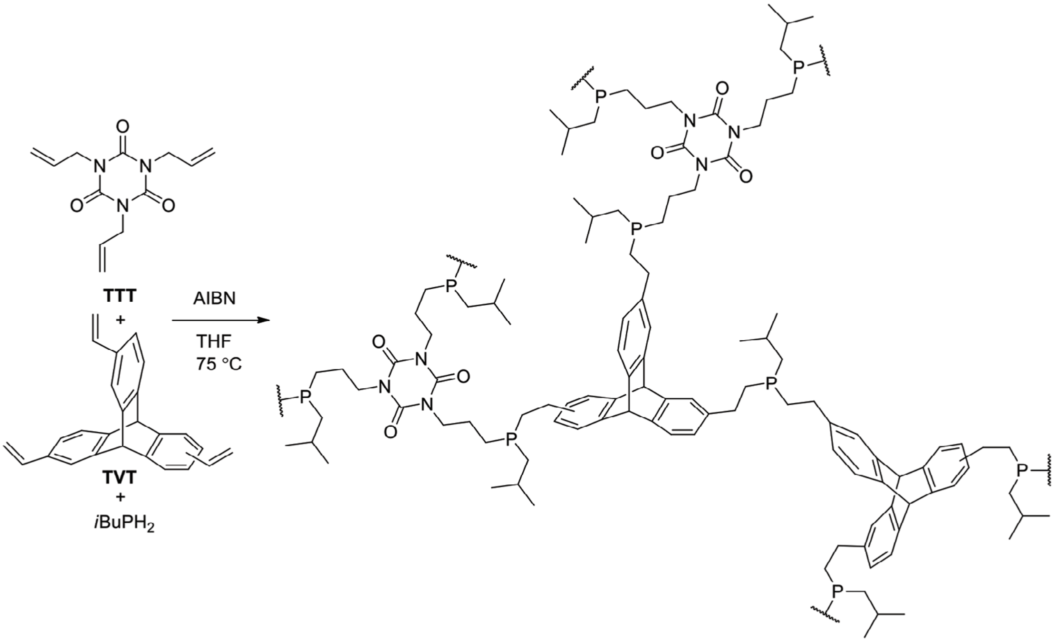
The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/macp.202400267

DOI: 10.1002/macp.202400267



Scheme 1. Synthesis of trivinyltriptycene (TVT).



Scheme 2. Representative synthesis of the (co)polymer networks prepared in this work. The relative quantities of the various components of the starting materials and purified networks are described in **Tables 1–3**.

unique bridgehead CH proton environments (δ_H = 5.77, 5.75, 5.74, 5.72) allowed us to conclude that this reaction produced 2,6,14- and 2,7,14-triformyltryiptycene in approximately a 3 to 1 ratio and an overall yield of 72% after purification using column chromatography (Figures S1 and S2, Supporting Information). We used this mixture of products in all subsequent studies and refer to the mixture of compounds as **TFT**. Conversion of **TFT** to **TVT** (isolated as a 4:1 mixture of the 2,6,14- and 2,7,14- isomers) was accomplished via a Wittig reaction employing methyltriphenylphosphonium bromide and potassium *t*-butoxide and resulted in a 77% yield after purification using column chromatography (Scheme 1, Figures S3 and S4, Supporting Information).

The preparation of (co)polymer networks (**PN1–PN5**) from different combinations of $i\mathrm{BuPH_2}$, **TTT**, and **TVT** was accomplished via thermally-initiated radical polymerization using azobisisobutyronitrile (AIBN) in a minimal amount of THF as outlined in **Scheme 2**. The ratios of each component were varied in order to achieve networks of only **TFT** or **TVT** as well as mixtures of **TFT**/**TVT**, where the relative amounts of each material took into consideration the relative olefin: P-H bond stoichiometry (**Table 1**). The reactions were carried out over 96 h, with 2 wt.% (with respect to $i\mathrm{BuPH_2}$) of AIBN added at t = 0, 24, 48, and 72 h. Given the sluggish reactivity observed and the potential hazards associated with the reactivity and toxicity of $i\mathrm{BuPH_2}$, the molecular and oligomeric materials that may be present within the (co)polymer networks were thoroughly removed. This was accomplished by aging each network (6 times) for 24 h in 5 mL of THF at which time no $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR resonances were observed for the resultant supernatants. The gel contents determined for the purified samples of **PN1–PN5** ranged from 59–98%.

Although (co)polymer networks **PN1–PN5** are formally insoluble, they swell in solvents such as $\mathrm{CDCl_3}$ which allows them to

Table 1. Molar ratios of starting materials used for the preparation of (co)polymer networks **PN1–PN5** and their respective gel contents.

	$^i\mathrm{BuPH_2}$	TVT	TTT	Gel Content
PN1	3	2	0	59%
PN2	3	1.5	0.5	79%
PN3	3	1	1	60%
PN4	3	0.5	1.5	66%
PN5	3	0	2	98%

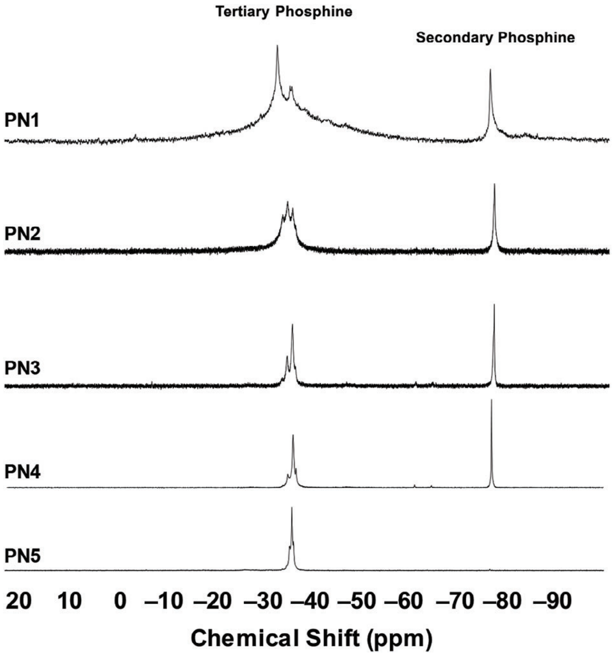


Figure 1. $^{31}P\{^1H\}$ NMR spectra of polymers **PN1–PN5** in $CDCl_3$.

be studied by NMR spectroscopy. The respective ^1H NMR spectra were broad (Figures S5–S9, Supporting Information), and thus, uninformative with respect to the detailed structure of the networks. The $^{31}P\{^1H\}$ NMR spectra provided useful information about the structure of the networks and the relative rates of hydrophosphination of **TTT** and **TVT** (**Figure 1**). **PN1** is derived exclusively from iBuPH$_2$ and **TVT** and its $^{31}P\{^1H\}$ NMR spectrum indicates the presence of both tertiary and secondary phosphine, with the latter implying incomplete hydrophosphination within the network. The relative quantities of **TTT** used to prepare (co)polymer networks **PN2–PN5** increases up to the extreme case of **PN5** which was produced using only **TTT** and iBuPH$_2$. In each network containing **TVT** a relatively small amount of secondary phosphine was present, as indicated by the observed resonance at ≈−75 ppm. This was not the case for network **PN5**, which was constructed from iBuPH$_2$ and **TTT** and showed no sign of secondary phosphine in its $^{31}P\{^1H\}$ NMR spectrum. This indicates that the hydrophosphination of **TTT** is more efficient than that of **TVT** in (co)polymer networks **PN1–PN5** despite the likelihood that **TTT**-rich networks are higher density than those that are **TVT**-rich.

To further study the impacts of the differing rates of hydrophosphination for **TTT** and **TVT**, we investigated the composition of the purified networks using a variety of elemental analysis techniques. We used elemental combustion analysis to determine C, H, and N content and inductively coupled plasma mass spectrometry (ICP-MS) to determine P content with the mass balance assumed to be made up by O (**Table 2**). In interpreting these data, a few specific considerations should be made. i) **TVT** has higher C and H content than **TTT**; ii) The only starting material containing N and O is **TTT**; and, iii) The only starting material containing P is iBuPH$_2$. For each purified network, the C composition is lower than anticipated indicating that **TVT** has been incorporated to a lesser extent than it was present in the starting materials. Furthermore, the N content for networks containing **TTT** is higher than predicted. This is also true for O, where the residual elemental compositions based on C, H, N, and P analysis implies O contents were higher than anticipated. This could indicate that the phosphines present in networks **PN1–PN5** were oxidized during the P analysis and that the P contents are thus underestimated. Figure S10 (Supporting Information) supports this claim and demonstrates the appearance of several NMR resonances consistent with the formation of phosphine oxides upon air exposure in the corresponding $^{31}P\{^1H\}$ NMR spectrum of **PN4**, chosen as a representative example.

With elemental analyses data in hand, we conducted a weighted fit for the three components (iBuPH$_2$, **TTT**, **TVT**) present in networks **PN1–PN5** to estimate their incorporation into the purified networks (**Table 3**). Consistent with the qualitative assessment outlined above, these fits indicate that the incorporation of **TVT** was systematically lower than anticipated and that the incorporation of **TTT** was systematically higher than expected. These conclusions are consistent with the observation noted above whereby the rate of hydrophosphination, based on the presence/absence of secondary phosphine in the respective $^{31}P\{^1H\}$ NMR spectra, appears to be much faster for **TTT** compared to **TVT**.

The thermal properties of networks **PN1–PN5** were investigated using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC; **Table 4**; **Figure 2**; Figures S11–S15, Supporting Information). The thermal stability of the networks varied significantly as a function of **TVT** and **TTT** content. The temperature of decomposition (T_d, taken at 2% mass loss in the respective TGA traces) for **PN1**, which is derived from iBuPH$_2$

Table 2. Elemental composition of (co)polymer networks **PN1–PN5**.

	C (wt.%)		H (wt.%)		N (wt.%)		P (wt.%)		O (wt.%)	
	Calc.[a]	Found[b]	Calc.[a]	Found[b]	Calc.[a]	Found[b]	Calc.[a]	Found[c]	Calc.[a]	Found[d]
PN1	82.18	80.85	7.81	7.74	0.00	0.44	9.95	10.83	0.00	0.14
PN2	76.55	72.69	7.89	8.36	2.35	2.78	10.41	9.50	2.69	6.67
PN3	70.46	61.96	7.99	8.37	4.93	6.89	10.92	11.62	5.63	11.16
PN4	63.71	57.91	8.09	8.29	7.77	8.25	11.48	11.67	8.88	13.88
PN5	56.22	55.20	8.20	7.94	10.93	11.18	12.10	7.89	12.49	17.79

[a] Calculated based on the elemental composition of the starting materials; [b] Determined by C,H,N combustion analysis; [c] Determined by ICP-MS; [d] Estimated based on unaccounted mass balance.

Table 3. Relative incorporation of *i*BuPH$_2$, TTT, and TVT in (co)polymer networks **PN1–PN5**.

		*i*BuPH$_2$ [wt.%]	TTT [wt.%]	TVT [wt.%]
PN1	Calculated[a]	29	0	71
	Found[b]	31	0	68
PN2	Calculated[a]	30	14	56
	Found[b]	28	17	52
PN3	Calculated[a]	32	29	39
	Found[b]	34	41	18
PN4	Calculated[a]	33	46	21
	Found[b]	34	49	13
PN5	Calculated[a]	35	64	0
	Found[b]	23	73	0

[a] Calculated based on the molar ratio of starting materials; [b] Determined from elemental analysis and ICP-MS data.

Table 4. Thermal properties of (co)polymer networks **PN1–PN5**.

Polymer Network	Temperature at 2% Mass Loss [°C]	Char Yield at 600 °C [%]	Glass Transition Temperature [°C]
PN1	301	37	–[a]
PN2	272	25	–[a]
PN3	257	18	86
PN4	237	18	67
PN5	189	13	65

[a] No obvious glass transition detected.

and **TVT**, was 301 °C, and the char yield at 600 °C was 37%. These values decreased in a stepwise fashion as the amount of **TTT** incorporated increased to a minimum of 189 °C and 13% for **PN5**, which contained only *i*BuPH$_2$ and **TTT**. The DSC data revealed a lower degree of mobility in the mobile state for networks containing relatively higher amounts of **TVT**. Glass transitions were not observed for **PN1** and **PN2** and the glass transition temperatures (T_g) decreased from 86 °C for **PN3** to 67 °C for **PN4** and 65 °C, with the latter being comprised solely of *i*BuPH$_2$ and **TTT**.

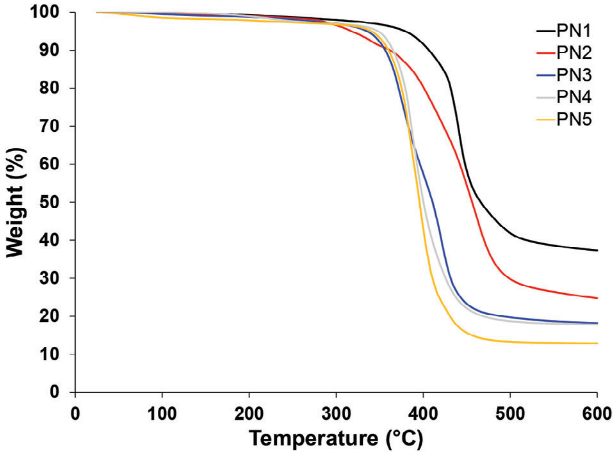


Figure 2. Thermal gravimetric analysis data for (co)polymer networks **PN1–PN5**.

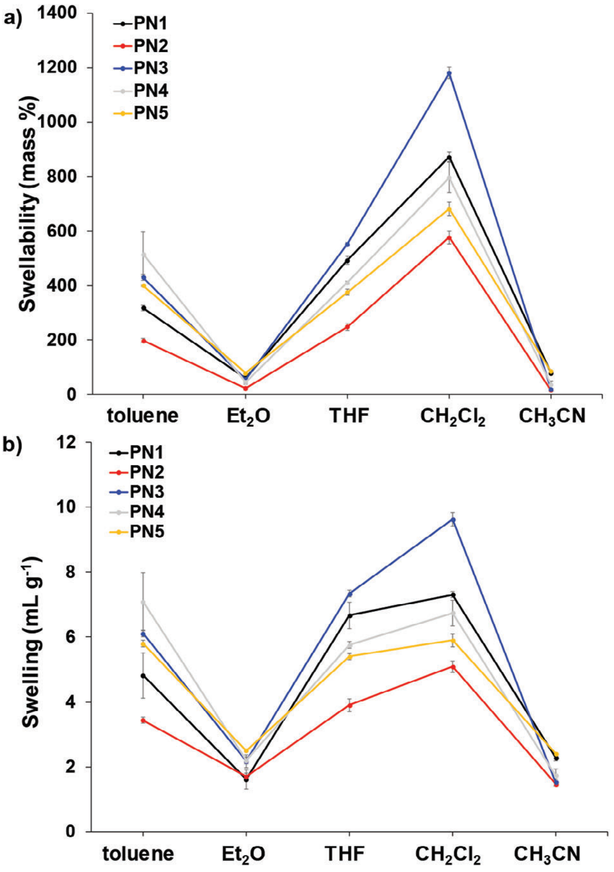


Figure 3. Swelling characteristics of (co)polymer networks **PN1–PN5** expressed as an increase in (a) mass and (b) volume.

To test the swellability of (co)polymer networks **PN1–PN5**, the samples were aged in a variety of solvents, and the mass of solvent incorporated into the resulting swollen polymer networks was measured (**Figure 3**). The volume of solvent incorporated into the polymer network was determined using the respective solvent densities. **TVT** is comprised of a relatively non-polar hydrocarbon with a rigid 3D structure while **TTT** contains some polar functional groups and is likely to adopt a relatively flat structure within the networks. Inspection of the data presented in Figure 3 revealed two interesting features: i) Despite the different structural features of **TVT** and **TTT**, all networks swelled most dramatically in toluene and solvents with moderate polarity (THF, CH$_2$Cl$_2$). Et$_2$O and CH$_3$CN were not efficiently incorporated into the networks; and, ii) There was no obvious trend in swellability as a function of **TVT** incorporation, indicating that its rigid, non-planar structure did not dramatically affect solvent incorporation and that the swellability of these three-component systems studied may be more complex than a simple consideration of the building blocks employed.

3. Conclusion

In this paper we describe an improved and optimized synthesis of **TFT**, which affords a mixture of two isomers on scales that are amenable to its use in the polymer materials arena. **TFT** was subsequently converted to **TVT** which was incorporated into polymer networks containing *i*BuPH$_2$ and varying ratios of **TVT** and **TTT**. Our network syntheses indicated that **TVT** undergoes hydrophosphination at a slower rate than **TTT**. Thermal analyses indicated that both thermal stability and glass transition temperature decreased as the concentration of **TTT** was increased in the networks. Finally, despite the differences in the structures of **TVT** and **TTT**, we found that the swellability of the networks prepared did not follow an obvious trend in relation to **TVT**/**TTT** content and that all of the networks described swelled significantly in toluene and moderately polar solvent such as THF and CH_2Cl_2. These findings will inform the design of future (co)polymer networks prepared via the phosphane-ene and analogous E-H bond addition reactions, and emphasizes the need for find tuning of the structure-property relationships associated with each starting material in such systems.

4. Experimental Section

General Considerations: All manipulations were carried out in an inert atmosphere and were performed either in a nitrogen-filled MBraun LabMaster 130 glovebox or on a Schlenk line. The solvents used were obtained from Caledon, Sigma-Aldrich, or Alfa-Aesar, and were dried using an MBraun-controlled atmosphere solvent purification system. They were then stored in Strauss flasks under a nitrogen atmosphere and over 3 Å (CH_3CN) or 4 Å molecular sieves. With the exception of *i*BuPH$_2$, which was donated by Solvay (now Syensqo), all chemicals were obtained from Sigma-Aldrich, Solvay, Fisher Scientific, or Aablocks and were used without further purification.

NMR spectra were acquired using Bruker 600 MHz, INOVA 600 MHz, or Bruker 400 MHz NMR spectrometers. The acquired ^{1}H and ^{13}C spectra were referenced internally using the residual proteo-solvent relative to tetramethylsilane at δ_H and $\delta_C = 0$. ^{31}P{^{1}H} NMR spectra were referenced externally to 85% phosphoric acid at $\delta_P = 0$. The reported data includes the chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, br = broad), coupling constants in Hertz, integration, and assignment. Mass spectrometry studies were conducted using a Bruker MicrO TOF II instrument. FT-IR (ATR) data was obtained using a Bruker ALPHA II FT-IR spectrometer. UV-Vis absorption spectra were recorded on a Cary 5000 UV-Vis-NIR spectrophotometer. Molar extinction coefficients were determined from the slope of a plot of absorbance against concentration using four solutions with known concentration. Thermogravimetric analysis (TGA) was performed to determine ceramic yields, using Mettler Toledo TGA instruments. ≈7 mg samples were placed in a platinum crucible and heated from 30 to 600 °C at a rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) was carried out using a Mettler Toledo DSC instrument under a nitrogen atmosphere, using an aluminum pan with a heating rate of 40 °C min^{-1}. Data was collected during the third heating cycle.

Synthesis of TFT: In a 1 L flask immersed in a cooler equipped with cooling coils attached to a refrigeration bath circulator triptycene (1.0 g, 3.9 mmol) was dissolved in CH_2Cl_2 (500 mL) and cooled to −15 °C. $TiCl_4$ (11.2 g, 6.50 mL, 59.0 mmol) and 1,1-dichlorodimethyl ether (6.7 g, 5.3 mL, 59 mmol) were then added sequentially to the mixture drop-wise by syringe. After the addition of $TiCl_4$, the reaction mixture turned red and then, after the addition of 1,1-dichlorodimethyl ether, turned dark green. The mixture was cooled and stirred at −15 °C under an argon atmosphere for 48 h. Another portion of $TiCl_4$ (3.7 g, 2.2 mL, 20 mmol) and 1,1-dichlorodimethyl ether (2.2 g, 1.8 mL, 20 mmol) were then added to the mixture followed by stirring at −15 °C for an additional 48 h. The reaction flask was then warmed up to 25 °C and a cold saturated solution of ammonium chloride in water (200 mL) was added, and the mixture was stirred until the red color sequentially turned to bright green and then yellow. The organic phase was then collected and washed with brine (2 × 100 mL) before it was dried with $MgSO_4$ and filtered. The volatile organics were removed *in vacuo* and the crude product was purified by column chromatography with silica gel (two consecutive columns: 1:4 v/v THF/hexanes, $R_f = 0.15$ then 1:2 v/v acetone/hexanes, $R_f = 0.33$) and gave **TFT** as bright yellow fluffy solid (0.80 g, 2.5 mmol, 63%). Melting point > 280 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 9.95$ (s, 6H), 7.98 (s, Ar, 6H), 7.94 (s, Ar, 12H), 5.72 (s, 1H), 5.74 (s, 1H), 5.75 (s, 1H), 5.77 (s, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): $\delta = 191.3$, 150.3, 149.7, 149.2, 144.9, 144.3, 143.8, 134.7, 134.7, 134.6, 130.0, 129.7, 129.4, 124.8, 124.7, 124.6, 123.9, 123.8, 123.7, 54.4, 54.1, 53.7, 53.4. FT-IR (ATR, cm^{-1}) = 2820, 2731, 1683, 1615, 1600, 1574, 1425, 1213, 1110, 840, 620, 753, 731, 688, 541, 519. UV−vis in CH_2Cl_2: $\lambda_{max} = 231$ nm ($\epsilon = 39700$ M^{-1} cm^{-1}), $\lambda_{max} = 257$ nm ($\epsilon = 29200$ M^{-1}cm^{-1}), $\lambda_{max} = 269$ nm ($\epsilon = 26700$ M^{-1} cm^{-1}), $\lambda_{max} = 302$ nm ($\epsilon = 8500$ M^{-1} cm^{-1}). Mass Spec. (ESI, +ve mode): exact mass calculated for $[C_{23}H_{14}O_3Na]^+$, $[M+Na]^+$: 361.0841; exact mass found: 361.0835.

Synthesis of TVT: **TFT** (0.50 g, 1.5 mmol), methyltriphenylphosphonium bromide (3.2 g, 8.9 mmol), and KO*t*Bu (2.32 g, 20.7 mmol) were dissolved in anhydrous THF (500 mL) and the mixture was heated to 65 °C and stirred for 48 h. The mixture was collected and washed with deionized H_2O (3 × 100 mL) and brine (100 mL). The organic phase was dried with $MgSO_4$ and filtered before the volatile organics were removed *in vacuo* and the crude product was purified by column chromatography with silica gel (1:2 v/v acetone/hexanes, $R_f = 0.75$) to give **TVT** as a colorless oil (0.38 g, 1.1 mmol, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.51$ (s, 6H), 7.36 (dd, *J* = 7.5, 3.3 Hz, 6H), 7.05 (d, *J* = 7.9 Hz, 6H), 6.67 (dd, *J* = 17.6, 10.9 Hz, 6H), 5.70 (d, *J* = 17.6 Hz, 6H), 5.41 (s, 1H), 5.42 (s, 1H), 5.44 (s, 1H), 5.45 (s, 1H), 5.19 (d, *J* = 10.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) $\delta = 136.7$, 136.6, 135.0, 133.8, 133.7, 128.7, 128.5, 128.50, 125.3, 123.9, 123.8, 123.7, 123.6, 121.1, 121.0, 54.2, 53.9, 53.8, 53.6. FT-IR (ATR, cm^{-1}) = 3086, 2985, 2952, 1679, 1444, 1407, 1345, 1318, 1278,1106, 990, 927, 762, 650, 545, 488, 453. UV−Vis in CH_2Cl_2: $\lambda_{max} = 239$ nm ($\epsilon = 85900$ M^{-1} cm^{-1}), 253 ($\epsilon = 89300$ M^{-1} cm^{-1}), $\lambda_{max} = 274$ nm, $\lambda_{max} = 299$ nm, $\lambda_{max} = 305$ nm ($\epsilon = 20900$ M^{-1} cm^{-1}). Mass Spec. (ESI, +ve mode): exact mass calculated for $[C_{26}H_{20}Na]^+$, $[M+Na]^+$: 355.1463; exact mass found: 355.1484.

Preparation of (Co)Polymer Networks PN1–PN5: A 20 mL pressure tube, equipped with a magnetic stir bar, was charged with *i*BuPH$_2$, **TVT**/**TTT**, and 0.2% wt. of AIBN based on ^{i}BuPH$_2$ (0.006 mmol). To create a homogeneous mixture, 2 mL of anhydrous THF was added. The resulting solution was a clear pale-yellow color. The tube was securely sealed and heated to 75 °C. The reaction mixture was stirred overnight at which time the solutions containing **TVT** were pale pink and had a gel-like consistency, while the one containing only **TTT** was colorless and gel-like. To ensure the completion of the reaction, the addition of AIBN with stirring at 75 °C for 24 h was repeated thrice more before the volatiles were removed under vacuum at 100 °C for 8 h. The polymer networks, **PN1–PN5** were then aged in 5 mL of THF six times to remove any unreacted phosphine-containing materials and to determine their gel content. After drying under vacuum at 100 °C overnight, the following characterization data was collected.

Characterization Data for (Co)Polymer Networks PN1–PN5: **PN1**: 1.03 g (59% gel content) from 0.50 g *i*BuPH$_2$, 1.22 g **TVT**, and catalytic AIBN (4 × 0.0018 g). ^{31}P{^{1}H} NMR (161.8 MHz): $\delta = -76.1, -35.4, -35.1, -32.5$; FT-IR (ATR, cm^{-1}): 2954, 2870, 1675, 1448, 1366, 1317, 992, 930, 762, 532; T_d (at 2% mass loss) = 301 °C. No obvious T_g was observed.

PN2: 1.43 g (79% gel content) from 0.52 g *i*BuPH$_2$, 0.92 g **TVT**, 0.23 g **TTT**, and catalytic AIBN (4 × 0.0018 g). ^{31}P{^{1}H} NMR (161.8 MHz): $\delta = -76.3, -35.2, -34.6, -33.5, -32.6$; FT-IR (ATR, cm^{-1}): 2954, 2863, 1678, 1454, 1363, 1262, 1100, 1063, 1050764, 632, 477. T_d (at 2% mass loss) = 272 °C. No obvious T_g was observed.

PN3: 1.15 g (60% gel content) from 0.50 g *i*BuPH$_2$, 0.61 g **TVT**, 0.46 g **TTT**, and catalytic AIBN (4 × 0.0018 g). ^{31}P{^{1}H} NMR (161.8 MHz):

$\delta = -76.1, -76.3\ -35.2, -34.5, -33.4$; FT-IR (ATR, cm^{-1}): 2956, 2869, 1676, 1456, 1369, 1320, 1159, 920, 718, 723, 640, 531. T_d (at 2% mass loss) = 257 °C. $T_g = 86$ °C.

PN4: 1.26 g (66% gel content) from 0.50 g *i*BuPH$_2$, 0.31 g **TVT**, 0.69 g **TTT**, and catalytic AIBN (4 × 0.0018 g). $^{31}P\{^1H\}$ NMR (161.8 MHz): $\delta = -76.3, -35.2, -34.6, -33.5$; FT-IR (ATR, cm^{-1}): 2954, 2867, 1674, 1456, 1369, 1322, 1159, 1021, 918, 799, 762, 723, 640, 529; T_d (at 2% mass loss) = 237 °C. $T_g = 67$ °C.

PN5: 1.48 g (98% gel content) from 0.47 g *i*BuPH$_2$, 0.92 g **TTT**, and catalytic AIBN (4 × 0.0018 g). $^{31}P\{^1H\}$ NMR (161.8 MHz): $\delta = -35.0, -35.1, -35.5, -35.8$; FT-IR (ATR, cm^{-1}): 2954, 2867, 1670, 1448, 1365, 1322, 1151, 1011, 764, 527; T_d (at 2% mass loss) = 189 °C. $T_g = 65$ °C.

Swellability Studies: To test the swellability of (co)polymer networks **PN1–PN5** a known mass of each dried network was placed in ~ 5 mL of solvent and aged overnight. The swollen polymer was then removed from solution, patted dry, and weighed. The %mass increase was determined by the following equation where M_s is the mass of the swollen network and M_i is the mass of the dry network.

$$\text{Swelling (\% Mass)} = (M_s - M_i/M_i) \times 100 \quad (1)$$

The volume of solvent incorporated into the swollen networks was calculated from the mass of the solvent determined in the studies above and the densities of the solvents employed. Statistics were calculated from experiments conducted in triplicate.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors gratefully acknowledge the Nuclear Waste Management Organization (NWMO, Toronto, Canada), the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canada Foundation for Innovation (CFI), Ontario Research Fund – Research Excellence (ORF-RF), and Solvay (now Syensqo) for funding and material support.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

phosphane-ene, polymer networks, polymer swelling, triptycene

Received: July 26, 2024
Revised: September 15, 2024

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