

Table S2. Methods of synthesis of diethynylarenes polymers and the type of their intramolecular structure. ^a

The Spacer Ar Structure	Synthesis Conditions or the Catalyst Used	Declared Type of Structure	Original Authors Notes	References in Main Text
-Ph-Ph-	$[(RO)_3P]_n-CoHal$, R = $Alk_{C\leq 6}$, n=1-4, Hal = Cl, Br, I	Crosslinked	Contains phenylene fragments	[64,71] 64. Korshak, V.V.; et al. US Patent US-3705131-A, filed 27.11.1970, and issued 1972. 71. Korshak, V.V., et al. <i>Dokl. Akad. Nauk SSSR</i> 1971 , <i>201</i> , 112.
-Ph-Ph-	i-Bu ₃ Al-TiCl ₄	Crosslinked	Contains phenylene fragments	[148] 148. Sergeyev, V.A.; et al. <i>Polymer Science U.S.S.R.</i> 1980 , <i>22</i> , 2130–2135, doi:10.1016/0032-3950(80)90075-1.
-Ph-Ph-	$[Rh(cod)Cl]_2$ и $[Rh(cod)im]$ (cod = cis,cis-cyclo-octadiene; im = imidazole)	Crosslinked	The presence of lath- eral groups –C ₆ H ₄ C ₆ H ₄ C≡CH	[18] 18. Bolasco, A.; et al. <i>Polymer</i> 1992 , <i>33</i> , 3049–3054, doi:10.1016/0032-3861(92)90094-D.
-Ph-Ph-	$[Pd(PPh_3)_2Cl_2]$ и $[Pd(PPh_3)_2(DEDP)_2]$	Crosslinked	The presence of lath- eral groups –C ₆ H ₄ C ₆ H ₄ C≡CH	[18] 18. Bolasco, A.; et al. <i>Polymer</i> 1992 , <i>33</i> , 3049–3054, doi:10.1016/0032-3861(92)90094-D.
-Ph-Ph-	Thermal polymerization	Often crosslinked	Absence of groups –C≡CH	[18] 18. Bolasco, A.; et al. <i>Polymer</i> 1992 , <i>33</i> , 3049–3054, doi:10.1016/0032-3861(92)90094-D.
-Ph-Ph-	$[Rh(cod)acac]$ and $[Rh(nbd)acac]$ (cod: cycloocta-1,5-diene; nbd: norborna-2,5-diene; acac: acetylacetonate)	Crosslinked	Cross-linking with arylene linkers. Polymers contain –C≡CH groups	[14] 14. Hanková, V.; et al. <i>Macromol. Rapid Commun.</i> 2012 , <i>33</i> , 158–163, doi:10.1002/marc.201100599.
-Ph-Ph-	Co ₂ (CO) ₈	Often crosslinked by a cyclopolymerization reaction	Absence of groups –C≡CH. The presence of 1,3,5-phenylene bridges.	[112] 112. Yuan, S.; et al. <i>Chem. Commun.</i> 2010 , <i>46</i> , 4547, doi:10.1039/c0cc00235f.
-Ph-Ph-	Annealing at 100 °C on Au(111) substrate	-	Forming of 2D networks on the Au(111) substrate	[19] 19. Zhou, H.; et al. <i>J. Am. Chem. Soc.</i> 2014 , <i>136</i> , 5567–5570, doi:10.1021/ja501308s.
-Ph-Ph-	Thermal polymerization	-	Precursor of carbon/carbon composites	[12] 12. Bilow, N.; et al. <i>SAMPE J.</i> 1982 , <i>18</i> , 19–24.
-Ph-Ph-Ph-	$[(RO)_3P]_n-CoHal$, R = $Alk_{C\leq 6}$, n=1-4, Hal = Cl, Br, I	Crosslinked	Contains phenylene fragments	[64,71] 64. Korshak, V.V.; et al. US Patent US-3705131-A, filed 27.11.1970, and issued 1972. 71. Korshak, V.V., et al. <i>Dokl. Akad. Nauk SSSR</i> 1971 , <i>201</i> , 112–114.
Thiophenylene-2,5	$[Rh(nbd)acac]$	Crosslinked	Polyconjugated chains linked by thiophene-2,5-diyl bridges. The presence of –C≡CH groups.	[20] 20. Bondarev, D.; et al. <i>Eur. Polym. J.</i> 2017 , <i>92</i> , 213–219, doi:10.1016/j.eurpolymj.2017.04.042.

Thiophenylene-2,5	Co ₂ (CO) ₈	Crosslinked	Polycyclotrimerization with the formation of nodes of 1,2,4- and 1,3,5-substituted benzenes. The almost disappearance of groups –C≡CH	[20] 20. Bondarev, D.; et al. <i>Eur. Polym. J.</i> 2017 , <i>92</i> , 213–219, doi:10.1016/j.eurpolymj.2017.04.042.
Naphthylene-1,4	Photo polymerization of crystals	Soluble	Weak branching of polymer chains	[169,170] 169. Rohde, O.; et al. <i>Makromol. Chem.</i> 1978 , <i>179</i> , 1999–2011, doi:10.1002/macp.1978.021790813. 170. Rohde, O.; et al. <i>Makromol. Chem.</i> 1978 , <i>179</i> , 2013–2029, doi:10.1002/macp.1978.021790814.
Naphthylene-1,4	Photo polymerization in solution	Soluble	Weak branching of polymer chains	[169,170] 169. Rohde, O.; et al. <i>Makromol. Chem.</i> 1978 , <i>179</i> , 1999–2011, doi:10.1002/macp.1978.021790813. 170. Rohde, O.; et al. <i>Makromol. Chem.</i> 1978 , <i>179</i> , 2013–2029, doi:10.1002/macp.1978.021790814.
2,3-Dichloronaphthylene-1,4	Thermal polymerization	Soluble	Weak branching of polymer chains	[[169,170] 169. Rohde, O.; et al. <i>Makromol. Chem.</i> 1978 , <i>179</i> , 1999–2011, doi:10.1002/macp.1978.021790813. 170. Rohde, O.; et al. <i>Makromol. Chem.</i> 1978 , <i>179</i> , 2013–2029, doi:10.1002/macp.1978.021790814.
2,3-Dichloronaphthylene-1,4	Photo polymerization	Soluble	Weak branching of polymer chains	[169,170] 169. Rohde, O.; et al. <i>Makromol. Chem.</i> 1978 , <i>179</i> , 1999–2011, doi:10.1002/macp.1978.021790813. 170. Rohde, O.; et al. <i>Makromol. Chem.</i> 1978 , <i>179</i> , 2013–2029, doi:10.1002/macp.1978.021790814.
Naphthylene-1,8	MoCl ₅ or WCl ₆	Partially soluble	Cyclization of –C≡CH groups to form a “semi-ladder” polymer with a conjugated system	[171] 171. Cho, H.N.; et al. <i>Polymer Bulletin</i> 1995 , <i>34</i> , 125–132, doi:10.1007/BF00316386.
Naphthylene-1,8	PdCl ₂	Soluble	Cyclization of –C≡CH groups to form a “semi-ladder” polymer with a conjugated system	[171] 171. Cho, H.N.; et al. <i>Polymer Bulletin</i> 1995 , <i>34</i> , 125–132, doi:10.1007/BF00316386.
Naphthylene-1,8	MoCl ₅ /EtAlCl ₂ (1:4) и WC1 ₆ /(n-Bu) ₄ Sn (1:4)	No information	Probably, occur cyclization of –C≡CH groups to form a “semi-ladder” polymer with a conjugated system	[171] 171. Cho, H.N.; et al. <i>Polymer Bulletin</i> 1995 , <i>34</i> , 125–132, doi:10.1007/BF00316386..
Naphthylene-2,6	TaCl ₅ /Ph ₄ Sn	Insoluble	Hyperbranched cross-linked polycyclotrimers; there are few groups –C≡CH	[116] 116. Zukal, A.; et al. <i>Macromol. Chem. Phys.</i> 2013 , <i>214</i> , 2016–2026, doi:10.1002/macp.201300317.
Антрилен-2,6	TaCl ₅ /Ph ₄ Sn	Insoluble	Hyperbranched cross-linked polycyclotrimers; there are few groups –C≡CH	[116] 116. Zukal, A.; et al. <i>Macromol. Chem. Phys.</i> 2013 , <i>214</i> , 2016–2026, doi:10.1002/macp.201300317.
-Ph-O-Ph-	Thermal polymerization	-	Precursor of carbon/carbon composites	[12] 12. Bilow, N.; et al. <i>SAMPE J.</i> 1982 , <i>18</i> , 19–24.

-Ph-O-Ph-	Thermal polymerization in melt	Soluble	Linear polyene; in each link the group $-C_6H_4OC_6H_4C\equiv CH$	[172] 172. Ratto, J.J.; et al. <i>J. Polym. Sci. Polym. Chem. Ed.</i> 1980 , <i>18</i> , 1035–1046, doi:10.1002/pol.1980.170180322.
-Ph-O-Ph-	$[(C_2H_5O)_3P]_4CoBr$	Insoluble	Polycyclotrimer	[66] 66. Korshak, V.V.; et al.. US Patent US-3705131-A, filed 27.11.1970, and issued 1972.
-Ph-O-Ph-	$i-Bu_3Al-TiCl_4$	Insoluble	Polycyclotrimer	[152] 15. Sergeyev, V.A.; et al. <i>Polymer Science U.S.S.R.</i> 1980 , <i>22</i> , 2130–2135, doi: 10.1016/0032-3950(80)90075-1.
-Ph-Si(C _n H _{2n+1}) ₂ -Ph-	TaBr ₅	Hyperbranched, soluble	The almost disappearance of groups $-C\equiv CH$	[173] 173. Liu, J.; et al. <i>Macromolecules</i> 2007 , <i>40</i> , 7473–7486, doi:10.1021/ma071062d.
-Ph-CH ₂ -Ph-	Thermal polymerization		Precursor of carbon/carbon composites	[12] 12. Bilow, N.; et al. <i>SAMPE J.</i> 1982 , <i>18</i> , 19–24.
-Ph-C(Ph)=C(Ph)-Ph-; -PhO(CH ₂) ₆ -OPh-; -CH ₂ OPh-CH ₂ -PhOCH ₂ -; -C(O)-PhO-(CH ₂) ₆ -OPh-C(O)-	InCl ₃ /2-iodophenol	Regioregular hyperbranched soluble polymers	Absence of groups $-C\equiv CH$	[174] 174. Wang, Z.; et al. <i>Polym. Chem.</i> 2014 , <i>5</i> , 5890–5894, doi:10.1039/C4PY00859F.

^a information is taken from the primary sources indicated in the last column