

Synthesis of Polymers Containing Polyaniline Fragments Linked by 1,4-Benzoquinone Groups

A. A. Durgaryan*, R. A. Arakelyan, and N. A. Durgaryan

Yerevan State University, ul. A. Manukyana 1, Yerevan, 375025 Armenia

*e-mail: durgaran@ysu.am

Received June 7, 2016

Abstract—Michael reaction of 1,4-benzoquinone and N-acetyl-4,4'-diaminodiphenylamine has afforded a new polymer; hydrolysis of the latter has yielded a product containing polyaniline fragments connected by 1,4-benzoquinone units in the backbone. The interaction of 1,4-benzoquinone and 1,4-phenylenediamine has afforded an earlier described polymer that has been characterized by IR and UV spectroscopy. Under the reaction conditions, 2,5-bis[(4-aminophenyl)amino]-1,4-benzoquinone prepared from the mentioned compounds at a 3 : 2 molar ratio can exist in three tautomeric forms. Electroconductivity of the prepared polymers increases from $<10^{-10}$ to 10^{-6} S/cm with the growing degree of doping.

Keywords: polycondensation, aniline oligomer, electron absorption spectroscopy, NMR spectroscopy, 1,4-benzoquinone, Michael reaction

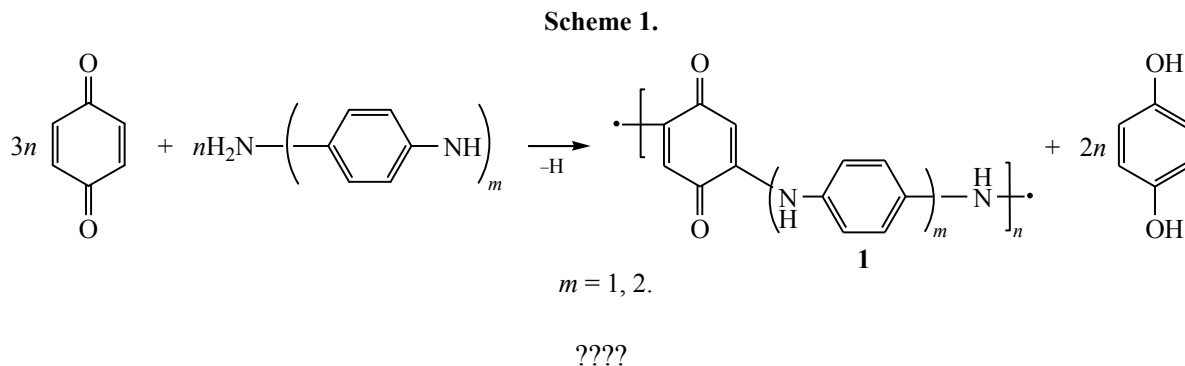
DOI: 10.1134/S1070363217010224

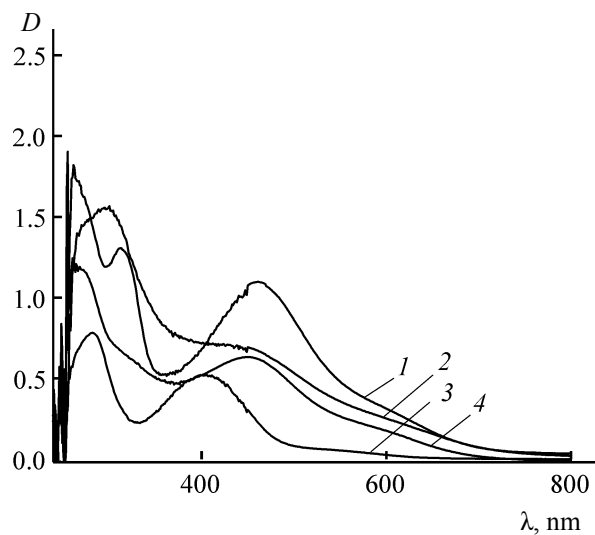
Polymers containing conductive units separated by different groups have been recently prepared to obtain new electroactive polymers exhibiting interesting properties. For example, polymers containing oligoaniline fragments connected via phenylenedisulfide [1], thiophene [2], and siloxane [3] groups have been described.

Quinone-containing polymers have been recognized for their interesting electrochemical [4] and photoconductor [5] properties. They play an important part in the understanding of biological processes [6–11] and have been applied in synthetic organic chemistry [12–14] as well as for preparation of magnetic [15] and electrode [16] materials. Polymers containing 1,4-benzoquinoneamine groups exhibit good adhesion to wet or rusty steel and can be used for the surface drying [17].

This study aimed to prepare and study polymers containing polyaniline fragments of different length and oxidation degree linked by 1,4-benzoquinone groups (Scheme 1).

The first member of the series ($m = 1$) (compound 1) is a product of the reaction between 1,4-benzoquinone and 1,4-phenylenediamine. This reaction in ethanol medium has been studied earlier [18]; the reaction has yielded a polymeric product poorly soluble in conventional organic solvents; it has been characterized by elemental analysis and electroconductivity data. We performed the synthesis reported in [18] in order to obtain UV-vis and IR spectra of the compound. The treatment of the obtained polymer with 5% aqueous solution of hydrochloric acid followed by washing with water, ethanol, and diethyl ether afforded





Electroconductivity of polymers **1**, **3**, and **4** as a function of degree of doping with iodine and the polymer–iodine molar ratio.

a polymer containing chloride ions. The polymer could be transformed in the basic form by treatment with 1 wt % aqueous solution of KHCO_3 . We also determined that the polymer solubility in 10 wt % KOH solution was about 10 g/L.

UV-vis (see figure) and IR (Tables 1 and 2) spectral data of the products corresponded to compound **1**.

We performed the reaction of 1,4-benzoquinone with 1,4-phenylenediamine at the 3 : 2 molar ratio under conditions of synthesis of polymer **1**, aiming to prepare 2,5-bis[(4-aminophenyl)amino]-1,4-benzoquinone **2** (Scheme 2).

The reaction product was a mixture of two fractions differing in the solubility in hot ethanol. ^1H NMR data for the obtained fractions revealed that the fraction with mp 255–256°C, readily soluble in hot ethanol, was likely a mixture of three tautomers (Scheme 3), whereas the poorly soluble fraction (mp >290°C) was mainly the quinoid form of the product.

Polymer **3** ($m = 2$) was prepared via the reaction of 1,4-benzoquinone with 4,4'-diamino-*N*-acetyldiphenylamine (Scheme 4). The structure of the product was confirmed by the data of NMR, IR (Table 1), and UV (see figure, Table 2) spectroscopy.

^1H NMR spectrum ($\text{DMSO}-d_6$) of polymer **3** contained the signals of protons E (1.9 ppm, $3.7/3 = 1.23$), A (5.8–6.1 ppm, $1.8/2 = 0.9$), C and D (6.5–7.5 ppm, $10/8 = 1.25$), B (9.40 ppm, $1.7/2 = 0.85$), and terminal amino groups (5.2–5.4 ppm, $0.4/4 = 0.1$). From the ratio of the average intensity of a non-terminal proton signal (1.25) and that for the terminal amino group proton (0.10), we could determine the polymerization degree ($n + 1$) of about 11. The

Table 1. IR spectroscopy data (cm^{-1}) for compounds **1–4**

Assignment	1	2	3	4
$\nu(\text{NH}_2, \text{terminal})$	3441 sh	3347 w, 3449	3446 sh	3433
$\nu(\text{NH}_{\text{sec}})$	3219	3223 v.w	3249 v.w	3271
$\nu(\text{Ar-H})$	3060 sh	3041 v.w, 3013 v.w	3060 v.w, 3040 v.w, 3020 v.w	
$\nu_{\text{s, as}}(\text{C-H})$			2924, 2852	
$\nu(\text{C=O}_{\text{acetate}})$			1663	
$\nu(\text{C=O}_{\text{quinone}})$	1641	1633 w	1646	1650
$\nu(\text{Ar})$	1511, 1416, 1385	1557, 1517 v.w, 1434 m, 1483 v.w	1575, 1509, 1414	1573, 1508, 1468
$\delta_{\text{as, s}}(\text{C-H})$			1382, 1370	
$\nu(\text{C-N}_{\text{phenyl}})$	1347, 1283	1359, 1278	1340, 1262	1374, 1285
$\nu(\text{C-N}_{\text{quinone}})$	1232, 1206		1227	1285
$\delta(\text{Ar-H}), \text{out-of-plane}$	1187, 1132, 1101, 1016	1191 v.w	1176, 1109, 1020	1141, 1179
$\delta(\text{C-H}), \text{out-of-plane}$	961, 899	689, 733	897, 728	670
$\delta(\text{Ar-H}), \text{out-of-plane}$	822	829	826	826

Table 2. UV-vis electron absorption spectroscopy data (λ_{\max} , nm) for compounds **1–4**

Assignment	1	2	3	4	2,5-Di(<i>p</i> -toluidino)-1,4-benzoquinone	2,5-Di(<i>p</i> -acetylaminoanilino)-1,4-benzoquinone [17]
1,4-Disubstituted benzene, $n > \pi^*$ -transition	270	266, 313	295	300	276	282
2,5-Disubstituted 1,4-benzoquinone, $\pi > \pi^*$ -transition	432	466	405	424	395	415

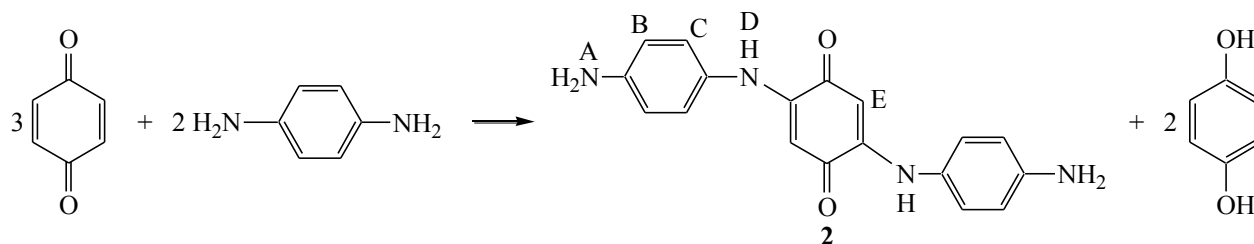
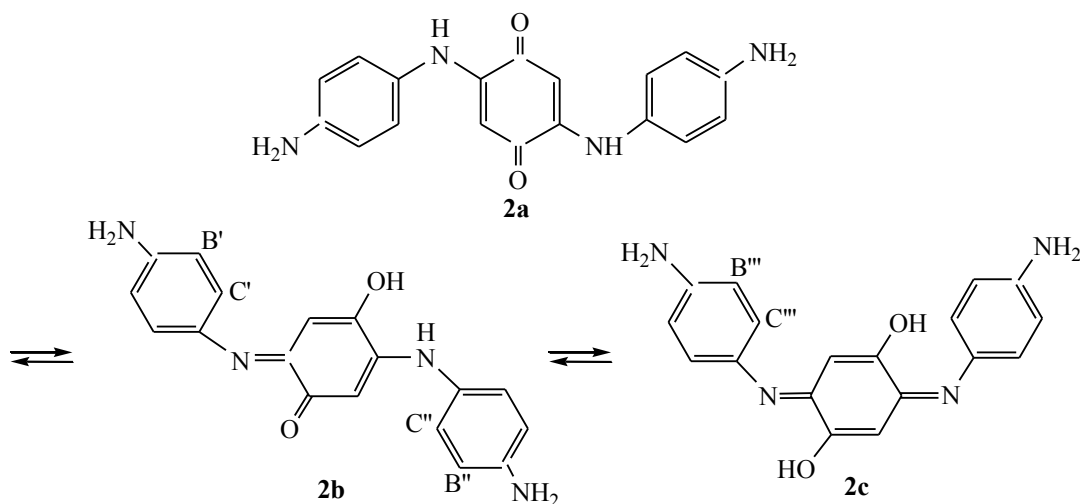
intensity of the signals of protons A and B (0.2) was somewhat weaker in comparison with other signals, due to the effect of terminal groups.

The hydrolysis of compound **3** afforded polymer **4** ($m = 2$) (Scheme 5); its structure was confirmed by the data of NMR, IR (Table 1), and UV (see figure and Table 2) spectroscopy.

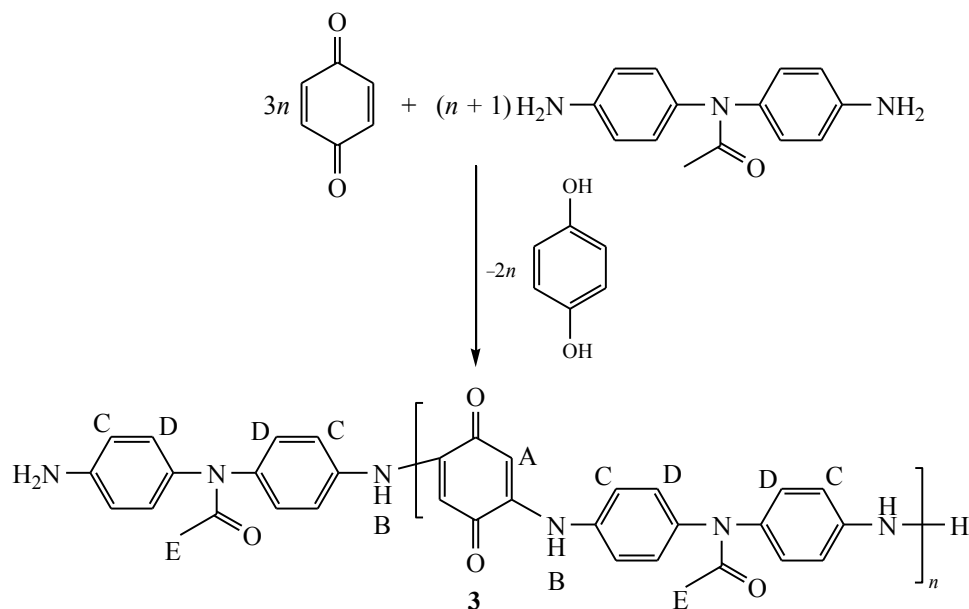
^1H NMR spectrum (DMSO- d_6) of polymer **4** contained the signals of NH_2 groups (5.1–5.3 ppm, $0.3/4 = 0.075$) and protons B (8.3–9.4 ppm, $1.4/2 = 0.70$). Chemical shifts of other protons ranged between 5.7 and 7.9 ppm ($10.9/11 = 0.91$). Again, the intensity of signals assigned to protons B was lower than that of other protons due to the influence of the terminal

groups. Average intensity of the signals of protons of aromatic and NH_2 groups for compound **4** equaled 0.94. Dividing that value by the intensity of signals per a proton of terminal amino group (0.075), we obtained the polymerization degree value ($n + 1$) = 12.6. The degrees of polymerization of polymers **3** and **4** were in agreement within the experimental accuracy limits.

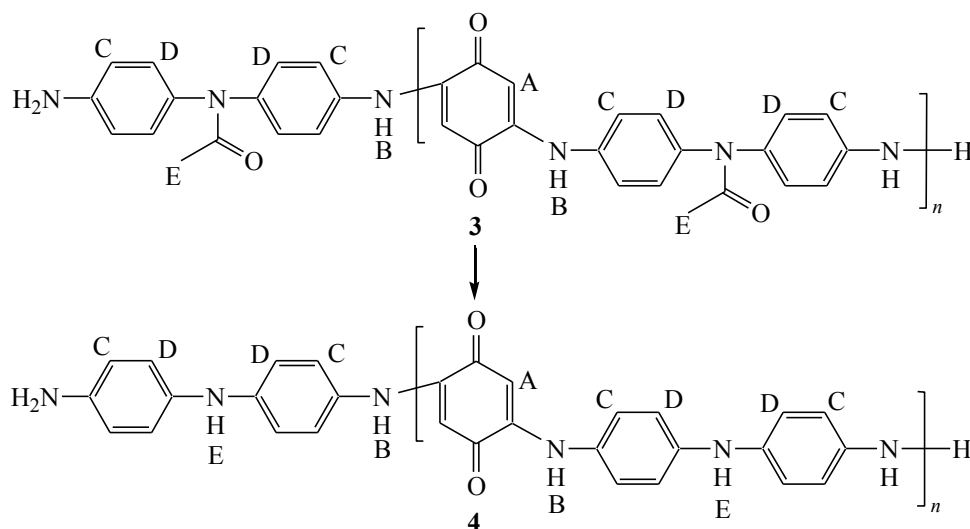
We determined electroconductivity of **1**, **3**, and **4** before and after doping with iodine (Table 3). It was found that the doping led to the increase in specific electroconductivity up to 10^{-6} S/cm. It should be noted that the highest electroconductivity of iodine-doped pernigraniline and emeraldine forms of polyaniline is of 10^{-4} and 10^{-3} S/cm, respectively [19, 20].

Scheme 2.**Scheme 3.**

Scheme 4.



Scheme 5.



In summary, we prepared new polymers with polyaniline fragments separated by 1,4-benzoquinone fragments starting from 1,4-benzoquinone and *N*-acetyl-4,4'-diaminodiphenylamine and studied them by means of NMR, IR, and UV spectroscopy.

EXPERIMENTAL

N-Acetyl-4,4'-diaminodiphenylamine (mp 195°C) and its precursors *N*-acetyldiphenylamine (mp 100–103°C) and *N*-acetyl-4,4'-dinitrodiphenylamine (mp 164–166°C) were prepared as described elsewhere [21–23].

1,4-Phenylenediamine (pure grade) was purified by sublimation (mp 143–145°C) and 1,4-benzoquinone (pure grade) was recrystallized from ethanol.

IR spectra (KBr) were recorded using a Nicolet Nexus FTIR spectrometer. ^1H NMR spectra were recorded using a Mercury 300 Varian NMR instrument (solution in $\text{DMSO-}d_6$, TMS as reference). UV-vis spectra were recorded using a Specord 50 spectrophotometer (solution in DMSO). Electroconductivity of the pelleted specimens was measured using an AT512 high-sensitivity Ohmmeter by a four-probe method.

Polymer 1 [18]. A solution of 1 g (9.3 mmol) of 1,4-phenylenediamine in 15 mL of ethanol was added at stirring to a boiling solution of 3 g (28 mmol) of 1,4-benzoquinone in 45 mL of ethanol. The obtained mixture was stirred during 45 min and left overnight. The precipitate was then filtered off, treated sequentially with hot ethanol (several times), hot 5 wt % solution of NaOH, and hot 5 wt % solution of HCl, and then washed with water till neutral reaction of the washings. Since the obtained polymer contained Cl^- ions, the precipitate was stirred with 120 mL of 1 wt % solution of KHCO_3 during 28 h, filtered off, washed with water till neutral reaction of the washings, and dried. Yield 1.9 g (90%). To obtain the basic form of the polymer, the procedure from [18] was adopted, and the target polymer was extracted from the reaction mixture with hot ethanol.

2,5-Bis[(4-aminophenyl)amino]-1,4-benzoquinone (2) was prepared similarly from 1.60 g (15 mmol) of 1,4-benzoquinone and 1.06 g (9.8 mmol) of 1,4-phenylenediamine. After the reaction was complete, the precipitate was filtered off, dried in air, and extracted with diethyl ether. The reaction product was divided in two fractions according to solubility in hot ethanol: a readily soluble part (0.65 g) and a poorly soluble one (0.89 g). The first fraction was recrystallized from ethanol (mp 255–256°C), and the second fraction was precipitated from DMF with water (mp >290°C). Yield 1.54 g (98%). ^1H NMR spectrum, δ , ppm: first fraction, 5.25 s (4H^{A}), 7.04 d [$1\text{H}^{\text{C(B)}}$, $J = 8.6$ Hz], 6.64 d [$1\text{H}^{\text{C(B)}}$, $J = 8.6$ Hz], 6.82 d. d [$1\text{H}^{\text{C(B)}}$, $J = 9.0$, 2.4 Hz], 6.93 d [$1\text{H}^{\text{C(B)}}$, $J = 9.0$ Hz], 7.02 d [$1\text{H}^{\text{C(B)}}$, $J = 8.6$ Hz], 7.04 d [$1\text{H}^{\text{C(B)}}$, $J = 8.6$ Hz], 5.30 s (1H^{E}), 5.48 s (1H^{E}), 7.43 d (1H^{D} , $J = 2.3$), 8.85 s (1H^{D}), 9.02 s (1H^{D}), 9.58 s (1H^{D}); second fraction, 5.32 s (4H^{A}), 6.62 d [$4\text{H}^{\text{C(B)}}$, $J = 8.7$ Hz], 7.04 d [$4\text{H}^{\text{C(B)}}$, $J = 8.7$ Hz], 5.52 s (1H^{E}), 5.60 s (1H^{E}), 5.72 s (1H^{E}), 5.83 s (2H^{E}), 9.02 s (1H^{D}), 9.10 s (1H^{D}), 9.33 s (2H^{D}).

Polymer 3 was prepared similarly from 0.67 g (6.3 mmol) of 1,4-benzoquinone and 0.5 g (2.1 mmol) of 4,4'-diamino-*N*-acetyldiphenylamine. After the reaction was complete, the precipitate was filtered off, washed several times with ethanol, dried in air, dissolved in DMSO, and precipitated with ethanol. The obtained precipitate was filtered off and dried at 314 K (0.2 kPa). Yield 0.54 g (75%).

Polymer 4. A mixture of 0.26 g (0.74 mmol) of compound **3** and 4.5 mL of 1.8 mol/L solution of

Table 3. Electroconductivity of polymers **1**, **3**, and **4** as a function of degree of doping with iodine and the polymer–iodine molar ratio

Polymer	Polymer : iodine	Doping degree	Specific electroconductivity, S/cm
1	1 : 0	–	$<10^{-10}$
	1 : 5	0.80	4.7×10^{-9}
	1 : 6	0.89	9.0×10^{-9}
3	1 : 0	–	$<10^{-10}$
	1 : 2.5	1.30	2.5×10^{-8}
	1 : 5	1.49	9.0×10^{-8}
4	1 : 6	1.50	2.1×10^{-7}
	1 : 0	–	$<10^{-10}$
	1 : 3	1.46	3.0×10^{-7}
	1 : 5	1.60	9.5×10^{-7}
	1 : 6	1.79	2.7×10^{-6}

NaOH in methanol was refluxed during 24 h under nitrogen. The obtained precipitate was filtered off, washed with methanol and then with water to neutral reaction of the washings, treated with 5 wt % of acetic acid solution, washed with water to neutral reaction of the washings, reprecipitated with diethyl ether from DMF, and dried first in a vacuum dessicator over P_2O_5 and then at 323 K (0.2 kPa). Yield 0.15 g (65%).

Doping with iodine. A required volume of 0.19 eq/L solution of iodine in CCl_4 was added to a weighed amount of a finely ground polymer. The mixture was left for 3–4 days at room temperature; the precipitate was filtered off and washed twice with a small volume of CCl_4 . The filtrate was titrated with 0.1 eq/L solution of sodium thiosulfate, and the precipitate was dried to a constant mass in a vacuum dessicator over P_2O_5 (0.2 kPa). The amount of iodine in the polymer specimen was calculated from the iodine consumption and the gain of the polymer mass. The doping degree was calculated as the molar ratio of iodine to the repeated unit of the polymer.

ACKNOWLEDGMENTS

This work was financially supported by State Committee for Science, Ministry of Education and Science of Armenia (project 15T-1D347).

REFERENCES

- Zhu, K., Wang, L., Jing, X., and Wang, F., *Macromolecules*, 2001, vol. 34, p. 8453. doi 10.1021/ma0108665.
- Buga, K., Pokrop, R., Majkowska, A., Zagorska, M., Planes, J., Genoud, F., and Pron, A., *J. Mater. Chem.*, 2006, vol. 16, p. 2150. doi 10.1039/B516677M
- Guo, Y., Mylonakis, A., Zhang, Z., Lelkes, P.I., Kalle, L.K., Li, Sh., Feng, Q., and Wei, Y., *Macromolecules*, 2007, vol. 40, p. 2721. doi 10.1021/ma0622985
- Bayen, S., Barooah, N., Sarma, R.J., Sen, T.K., Kar-makar, A., and Baruah, J.B., *Dyes Pigm.*, 2007, vol. 75, p. 1770. doi 10.1016/j.dyepig.2006.07.033
- Ishikita, H. and Knapp, E-W., *J. Am. Chem. Soc.*, 2005, vol. 127, p. 14714. doi 10.1021/ja052567r.
- Xu, M., Lukeman, M., and Wan, P., *Photochem. Photobiol.*, 2006, vol. 82, p. 50. doi 10.1562/2005-02-17-RA-444
- Cramer, W.A., Zhang, H., Yan, J., and Kurisu, G., *Biochem. Soc. Trans.*, 2005, vol. 33, p. 921. doi 10.1042/BST0330921
- Hartmut, M. and Johann, D., *Biochem.*, 1988, vol. 27, p. 1. doi 10.1021/bi00401a001
- Rutherford, W.A. and Anja, K.-L., *Trends Biochem Sci.*, 2001, vol. 26, p. 648. doi 10.1016/S0968-0004(01)01953-3
- Krieger, A. and Weis, E., *Photosynthetica*, 1992, vol. 27, p. 89.
- Rutherford, A.W. and Faller, P., *Philos. Trans. R. Soc. Lond. (B)*, 2003, vol. 358, p. 245. doi 10.1098/rstb.2002.1186.
- Grecian, S., Wroblewski, A.D., and Aube, J., *Org. Lett.*, 2005, vol. 7, p. 3167. doi 10.1021/ol050715c
- Bakola-Christianopoulou, M.N., *Appl. Organomet. Chem.*, 2001, vol. 15, p. 889. doi 10.1002/aoc.231
- Yamashita, H., Reddy, N.P., and Tanaka, M., *Organometallics*, 1997, vol. 16, p. 5223. doi 10.1021/om970215q
- Hasegawa, T., Mochida, T., Kondo, R., Kagoshima, K., Iwasa, Y., Akutagawa, T., Nakamura, T., and Saito, G., *Phys. Rev. (B)*, 2000, vol. 62, p. 10059. doi 10.1103/PhysRevB.62.10059
- Soriaga, M.P. and Hubbard, A.T., *J. Am. Chem. Soc.*, 1982, vol. 104, p. 2735. doi 10.1021/ja00374a008
- Nithianandam, V.S., Kaleem, K., Chertok, F., and Ephem, S., *J. Appl. Pol. Sci.*, 1991, vol. 42, p. 2893. doi 10.1002/app.1991.070421105
- Parini, V.P., Kazakova, Z.S., Okorokova, M.P., and Berlin, A.A., *Vysokomol. Soed.*, 1961, vol. 3, p. 402.
- Cao, Y., *Synth. Meth.*, 1990, vol. 35, p. 319. doi 10.1016/0379-6779(90)90216-8
- Xing-Rong Zeng and Tze-Man Ko, *J. Polym. Sci. (B)*, 1997, vol. 35, p. 1993. doi 10.1002/(SICI)1099-0488(19970930)35:13<1993::AID-POLB1>3.0.CO;2-O
- Berlin, A.A., *Zh. Obshch. Khim.*, 1944, vol. 14, p. 445.
- Gnehm, R. and Wedenberg, H., *Z. Ang. Chem.*, 1899, vol. 12, p. 1052.
- Beilstein III*, vol. 13, p. 113.