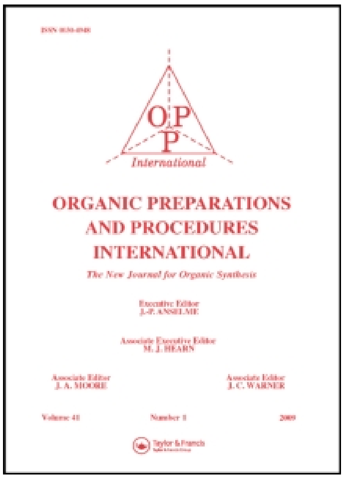


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

SYNTHESIS OF A NEW POLYMER POLY(4'-VINYLDIBENZO-14-CROWN-4)

T. C. Kuan[a]; S. J. Wang[a]
[a] Institute of Nuclear Energy Research, AEC, Lung-Tan, Taiwan REPUBLIC OF CHINA

To cite this Article Kuan, T. C. and Wang, S. J.(1984) 'SYNTHESIS OF A NEW POLYMER POLY(4'-VINYLDIBENZO-14-CROWN-4)', Organic Preparations and Procedures International, 16: 2, 140 — 143

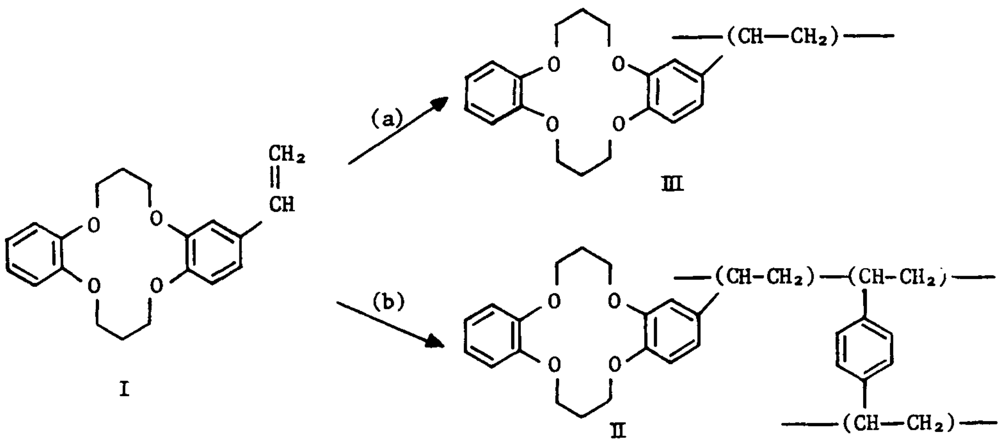
To link to this Article: DOI: 10.1080/00304948409356178

URL: http://dx.doi.org/10.1080/00304948409356178

SYNTHESIS OF A NEW POLYMER POLY(4'-VINYLDIBENZO-14-CROWN-4)

Submitted by T. C. Kuan and S. J. Wang*
(12/12/83)
Institute of Nuclear Energy Research
AEC Lung-Tan, Taiwan 325, REPUBLIC OF CHINA

Neutral macroheterocycles such as crown ethers and cryptands are noted not only for their powerful chelation of alkali and alkaline earth cations,[1] but also for their interaction with transition metal cations[2] and ions of the lanthanides series.[3] However, in order to facilitate their retrieval and to increase their effectiveness, the often toxic and rather expensive macrocycles have been incorporated into the backbone of an insoluble polymeric network[4,5] or attached as pendant moieties to the polymer chain.[6-8] We have reported the synthesis of dibenzo-14-crown-4 and derivatives,[9-12] which form 1:1 stable complexes with lithium ion. [12-14] We herein describe the syntheses of polymers from 4'-vinyldibenzo-14-crown-4 (I) (Scheme 1).[11] Catechol was converted to O-bis[(3-hydroxypropyl)oxy] benzene; chlorination of the latter with thionyl chloride followed by reaction with 4-formylcatechol gave the corresponding aldehyde. Treatment



Reagents: (a) AIBN, dry benzene, at 65°, 24 hrs. (b) 8% DVB, AIBN, dry benzene, at 65°, 24 hrs.

of the resulting aldehyde with methylmagnesium iodide gave the desired secondary alcohol, which was then dehydrated over alumina coated with sulfuric acid to yield I.

Polymerization of I was conducted in benzene with AIBN. The results are listed in the Table. The reaction was monitored by the disappearance of the characteristic vinyl bands at 1620 cm^{-1} (C=C stretch) and 1340 cm^{-1} are listed in the Table. The reaction was monitored by the disappearance of the characteristic vinyl bands at 1620 cm^{-1} (C=C stretch) and 1340 cm^{-1} (C-H bending) in the IR spectrum and by the absence of vinyl signal at δ 5.00 and 5.42 in ^{1}H-NMR spectrum. The average molecular weight of polymer could be increased by reducing the amount of AIBN under the same conditions (see Table). In the copolymerization of I with divinylbenzene (DVB), the monomer was polymerized to give a copolymer, cross-linked poly(4-vinyldibenzo-14-crown-4) (II), with broader dispersity or larger $\bar{M}w/\bar{M}n$ ratio in gel permeation chromatography (GPC) and with smaller average molecular weight than those of III. These powdered polymers did not display any crystallinity.[15]

The choice of solvents has also been investigated. Benzene was found to be superior to 1,4-dioxane, carbon tetrachloride (CCl_4), tetrahydrofuran (THF), or toluene. The pure polymers could be obtained by recrystallization from a co-solvent of chloroform-hexane to remove the unreacted monomer.

EXPERIMENTAL SECTION

Cross-linked Poly(4'-vinyldibenzo-14-crown-4)(II).- A solution of I (1.712 g, 5.25 mmol), divinylbenzene (DVB, 0.149 g, 1.143 mmol) and dry benzene (90 ml) was thoroughly degassed, added to a 150 ml flask containing α,α'-azobisisobutyronitrile (AIBN, 0.0324 g, 0.198 mmol); the flask was cooled

TABLE. Polymerization of I

Polymer	AIBN,% by mol	DVB,% by wt	Yield[a] %	Mn[b] ($x10^3$)	Mw/Mn[c]	mp. (°C)
II	3	8	53	3	2.44	139-150
III	3	0	56	5	1.34	120-124
III	2	0	52	7.3	1.63	140-146

---

a. Wt% against monomer charged.
b. By vapor pressure osmometry in toluene at 50°.
c. By GPC with THF at 30° as eluent and μ-styragel 10^5, 10^4, 10^3, 500 Å column and by using calibration curve for polystyrene.

in liquid nitrogen and then sealed under nitrogen atmosphere. The mixture was shaken at 65° for 24 hrs (shaker bath). After cooling to room temperature, the solution was slowly poured into 1 l. of n-hexane and the resulting white precipitate was collected and recrystallized from a mixture of 1:3 (V/V) chloroform-hexane to remove the unreacted monomer. The solid was finally dried under vacuum to give 0.986 g (53%) of II as a white powder. IR(KBr): 3060, 3030, 2920, 2870, 1600, 1500, 1470, 1430, 1390, 1260, 1130, 1160, 740 cm^{-1}; ^{1}HNMR (80 MHz, $CDCl_3$): δ 0.74-2.50 (broad, $PhCHCH_2$- and -$O-CH_2-\underline{CH_2}-CH_2-O-$), 3.68-4.52 (broad, $-O-\underline{CH_2}-CH_2-$), 5.89-7.26 (broad aromatic H).

Anal. Calcd for $(C_{20}H_{22}O_4)_{0.785}(C_8H_{10})_{0.215}$: C, 74.98; H, 7.02

Found: C, 75.09; H, 6.93

Poly(4'-vinyldibenzo-14-crown-4)(III).- A solution of I (1.828 g, 5.6 mmol) in dry benzene (90 ml) was added to a 150 ml flask containing AIBN (0.0284 g, 0.173 mmol) and polymerized as described in the proceding procedure to yield 1.02 g (56%) of white powdered product (III). IR(KBr): 3060, 3030, 2920, 2870, 1600, 1500, 1470, 1430, 1390, 1260, 1130, 1060, 740 cm^{-1}; ^{1}HNMR (80 MHz, $CDCl_3$): δ 0.74-2.50 (broad, 7, $Ph\underline{CHCH_2}$- and $-O-CH_2-\underline{CH_2}-CH_2-O-$), 3.67-4.52 (broad, 8, $-O-\underline{CH_2}-CH_2-$), 5.89-7.05 (broad 7, aromatic H).

Anal. Calcd for $(C_{20}H_{22}O_4)_x$: C, 73.59; H, 6.80

Found: C, 73.56; H, 6.75

REFERENCES

1. **N. S. Poonia and A. V. Bajaj, Chem. Rev., 79, 389 (1979).**
2. **E. Blasius and K. P. Janzen, Pure & Appl. Chem., 54, 2115 (1982).**
3. **J. Massaux and J. F. Desreux, J. Am. Chem. Soc., 104, 2967 (1982).**
4. **J. Smid, Ind. Eng. Chem. Prod. Res. Dev., 19, 364 (1980).**
5. **E. Blasius, K. P. Janzen, W. Adrian, G. Klantke, R. Loischeider, P. G. Maurer, V. B. Nguyen, T. Nguyen-Tien, G. Scholten and J. Stochemer, Z. Anal. Chem., 284, 337 (1977).**
6. **A. Warshawsky and N. Kahana, J. Am. Chem. Soc., 104, 2663 (1982).**
7. **A. Warshawsky and N. Kahana, Polym. Sci. Technol., 16, 227 (1982).**
8. **F. Montanari, J. Org. Chem., 46, 2125 (1981).**
9. **T. C. Kuan, C. L. Chiou and S. J. Wang, Syn. Commun., 12, 477 (1982).**
10. **C. S. Chen, S. J. Wang and S. C. Wu, Org. Prep. Proc. Int., 14, 350 (1980).**
11. **T. C. Kuan, C. L. Chiou and S. J. Wang, Polymer Bull., 9, 216 (1983)**
12. **C. S. Chen, S. J. Wang and S. C. Wu, J. Heterocyclic Chem., 20, 795 (1983).**
13. **G. Shoham, W. N. Lipscomb and U. Olsher, Chem. Commun., 208 (1983).**
14. **C. S. Chen, S. J. Wang and S. C. Wu, Submitted for publication.**
15. **S. Kopolow, T. E. Hogen Esch and J. Smid, Macromolecules, 6, 133 (1973).**