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Anionic Telomerizations of Styrene with Some Secondary Amines*[1]

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The anionic telomerizations of styrene with some secondary amines catalyzed by sodium metal were investigated. In this reaction a secondary amine was used as a telogen and styrene as a taxogen. Three telomers, *i. e.* *N,N*-disubstituted 2-phenylethylamine, *N,N*-disubstituted 2,4-diphenylbutylamine and *N,N*-disubstituted 2,4,6-triphenylhexylamine were separated from the mixture of the produced telomers under vacuum distillation. Proton NMR spectra of these telomers in carbon tetrachloride were consistent with the expected structural formulas. The reaction scheme was proposed to explain the formation of telomers.

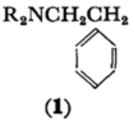
Anionic telomerization may be characterized to be an anionic polymerization of vinyl, vinylidene and diene compounds so that the initiation reaction, the propagation reaction and the chain transfer reaction can take place to a comparable extent in the polymerization reaction. If the propagation reaction exceeds the chain transfer one, polymerization reaction, in the ordinary sense, would occur to produce high polymers, and if the chain transfer reaction overcomes the propagation one, the anionic addition reaction would be realized. In fact many of the anionic addition reactions of vinyl and diene compounds with alkylaromatic compounds which contain the α-hydrogens in the side chain have been reported by Pine and his coworkers[1-11] and by other authors.[12-15]

The small unbalance between the rate constants of the initiation, the propagation and the chain transfer reactions can sometimes be compensated by controlling the concentrations of a telogen and a taxogen. In other words the molar ratio of a telogen to a taxogen during the telomerization reaction influences the composition and the average molecular weight of the produced telomers.

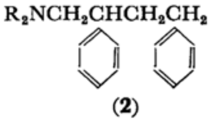
In this paper the results on the telomerization of styrene with some secondary amines, the separation of the telomers and NMR spectra of the separated telomers will be reported. The formation of the telomers will be discussed with the proposed reaction scheme.

Results and Discussion

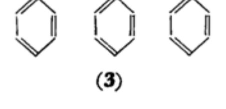
Reactions of Styrene with Secondary Amines. Secondary amines were subjected to reaction with styrene to produce telomers, from which were separated the telomers with $n=1$, 2 and 3, respectively, *i.e.* *N,N*-disubstituted 2-phenylethylamines (**1**), *N,N*-disubstituted 2,4-diphenylbutylamines (**2**) and *N,N*-disubstituted 2,4,6-triphenylhexylamine (**3**).



(**1**)



(**2**)



(**3**)

The higher homologs of these telomers were formed at the same time, but remained undistilled in residue under vacuum distillation. Diethylamine, di-*n*-propylamine, di-*n*-butylamine and diisobutylamine were reacted as a telogen. The reaction products obtained are listed in Table 1. The molar ratio of styrene to the amine influenced greatly the

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*[1] Anionic Telomerizations. II.

1) H. Pines, J. A. Vesely and V. N. Ipatieff, *J. Am. Chem. Soc.*, **77**, 554 (1955).

2) H. Pines and V. Mark, *ibid.*, **78**, 4316 (1956).

3) L. Schaap and H. Pines, *ibid.*, **79**, 4967 (1957).

4) H. Pines and L. Schaap, *ibid.*, **80**, 3076 (1958).

5) H. Pines and D. Wunderlich, *ibid.*, **80**, 6001 (1958).

6) H. Pines and D. Wunderlich, *ibid.*, **81**, 2568 (1959).

7) H. Pines and B. Notari, *ibid.*, **82**, 2209 (1960).

8) B. Notari and H. Pines, *ibid.*, **82**, 2945 (1960).

9) H. Pines and J. Shabtai, *J. Org. Chem.*, **26**, 4220 (1961).

10) H. Pines and N. C. Sih, *ibid.*, **30**, 280 (1965).

11) H. Pines and J. Oszczapowicz, *ibid.*, **32**, 3183 (1967).

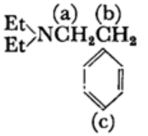
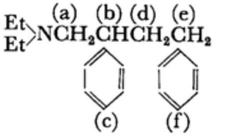
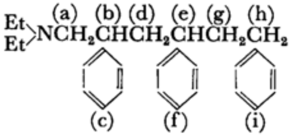
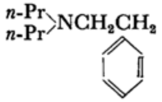
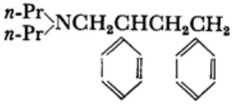
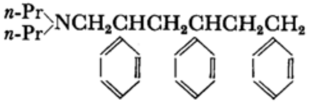
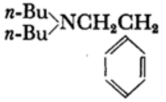
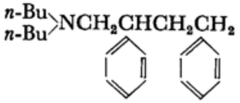
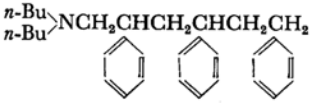
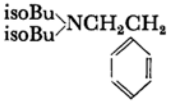
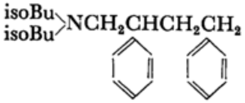
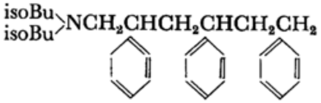
12) R. Wegler and G. Pieper, *Chem. Ber.*, **83**, 6 (1950).

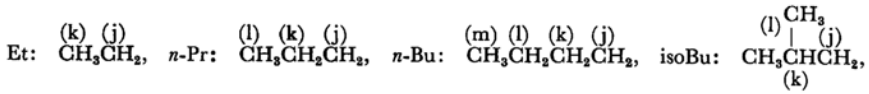
13) H. Hart, *J. Am. Chem. Soc.*, **78**, 2619 (1956).

14) R. D. Closson, J. P. Napolitano, G. G. Ecke and A. J. Kolka, *J. Org. Chem.*, **22**, 646 (1957).

15) G. G. Eberhardt and H. J. Peterson, *ibid.*, **30**, 82 (1965).

TABLE 1. TELOMERS OBTAINED IN THE TELOMERIZATION OF STYRENE WITH SECONDARY AMINES

Telogen	Telomer **1**		Telomer **2**		Telomer **3**	
Diethylamine		(**1a**)		(**2a**)		(**3a**)
Di-*n*-propylamine		(**1b**)		(**2b**)		(**3b**)
Di-*n*-butylamine		(**1c**)		(**2c**)		(**3c**)
Diisobutylamine		(**1d**)		(**2d**)		(**3d**)



$$\text{Et:}\ \overset{(k)}{CH_3}\overset{(j)}{CH_2},\quad n\text{-Pr:}\ \overset{(l)}{CH_3}\overset{(k)}{CH_2}\overset{(j)}{CH_2},\quad n\text{-Bu:}\ \overset{(m)}{CH_3}\overset{(l)}{CH_2}\overset{(k)}{CH_2}\overset{(j)}{CH_2},\quad \text{isoBu:}\ CH_3\underset{(k)}{\overset{\overset{(l)\,CH_3}{|}}{CH}}\overset{(j)}{CH_2},$$

TABLE 2. REACTION CONDITIONS AND REACTION PRODUCTS

Secondary amine reacted	Moles of reactants [Styrene]/[Amine]	Dropping time min	Reaction time and temp. min	Reaction time and temp. °C	Telomer **1**[a] %	Tolomer **2**[a] %	Tolomer **3**[a] %
Diethylamine	0.3/0.3	100	180	50.0±0.5	76.9	2.0	0
	0.6/0.3	30	180	50.0±0.5	39.7	6.9	6.2
	3.0/1.5	80	180	50.0±0.5	39.2	11.3	2.5
Di-*n*-propylamine	0.6/0.3	35	180	100.0±0.5	29.4	25.2	10.3
Di-*n*-butylamine	0.6/0.3	20	180	150.0±0.5	13.7	26.4	23.5
Diisobutylamine	0.54/0.27	24	180	120.0±0.3	8.5	30.6	18.0

a) Yields were calculated on the basis of styrene added.

compositions of telomers. Table 2 gives the reaction conditions and the reaction products. Column 1 lists the amines used, and columns 6, 7 and 8 report the yields of the separated telomers.

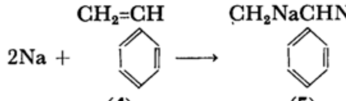
Structures of the Separated Telomers. The telomer **1a** has a methyl triplet (1 : 2 : 1) at 9.03 τ and a methylene quartet (1 : 3 : 3 : 1) at 7.52 τ. These are the typical signals of ethyl group and are assigned to the two equivalent ethyl groups of the telomer **1a**. The signal at 7.38 τ is that of the methylene protons (a) and (b) between the nitrogen atom and the phenyl group. The protons constituting the phenyl group show a singlet at 2.94 τ. The telomer **2a** gives the signals at 9.12, 2.92 and 2.99 τ which are assigned to methyl protons (k), phenyl protons (c) and phenyl protons (f), respectively. The signals due to five methylene and a methine groups were not assigned completely, but the signals at 7.45, 7.56, 7.68 and 7.80 τ seem to form a methylene quartet due to protons (j). The telomer **3a** shows a methyl triplet and three phenyl singlets at 9.16, 2.93, 2.96 and 3.01 τ which are assigned to protons (k), (c), (f) and (i), respectively. The NMR signals of other telomers were assigned, and the results on the assignments of the signals to the protons of the separated telomers **1**, **2** and **3** are listed in Table 3. It was confirmed from IR spectra that none of the separated telomers has a –NH– group. The results on the

Table 3. Assignment of the signals to the protons

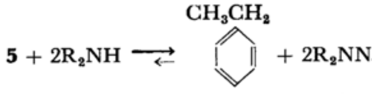
Telomers	The τ values of the signals of the protons in ppm												
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)	(m)
1a	7.38	7.38	2.94	—	—	—	—	—	—	7.33 7.45 7.56 7.68	8.91 9.03 9.15	—	
2a	···	···	2.92	···	···	2.99	—	—	—	7.45 7.56 7.68 7.80	9.00 9.12 9.24	—	
3a	···	···	2.93	···	···	2.96	···	···	3.01	7.54 7.56 7.68 7.80	9.03 9.16 9.27	—	
1b	7.34	7.34	2.84	—	—	—	—	—	—	7.48 7.59 7.71	8.40 8.52 8.65 8.76	9.03 9.15 9.27	
2b	···	···	2.81	···	···	2.88	—	—	—	···	8.49 8.61 8.74 8.86	9.12 9.23 9.35	
3b	···	···	2.79	···	···	2.85	···	···	2.91	···	8.52 8.64 8.77 8.89	9.14 9.26 9.37	
1c	7.39	7.39	2.86	—	—	—	—	—	—	···	···	···	9.03 9.13 9.23
2c	···	···	2.86	···	···	2.86	—	—	—	···	···	···	9.03 9.13 9.24
3c	···	···	2.87	···	···	2.87	···	···	2.87	···	···	···	9.03 9.14 9.23
1d	7.38	7.38	2.77	—	—	—	—	—	—	7.86 7.95	8.27	9.04 9.09 9.16 9.27	—
2d	···	···	2.78	···	···	2.86	—	—	—	7.94 8.03	8.40	9.05 9.13 9.25 9.36	—
3d	···	···	2.81	···	···	2.87	···	···	2.93	8.00 8.10	8.46	9.06 9.16 9.27 9.30 9.40	—

NMR and IR spectra of the produced telomers are consistent with the structural formulas of the telomers **1**, **2** and **3** listed in Table 1.

Reaction Scheme. The reaction scheme is considered as follows. The initiation reaction may be the addition of sodium to styrene (**4**), and the organometallic compounds **5** transmetalates with a secondary amine **6** to give the compound **7**.

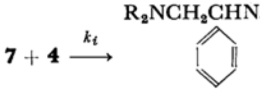


(**4**) (**5**) (1)



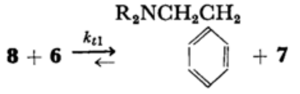
(**6**) (**7**) (2)

The compound **7** is able to react with styrene.

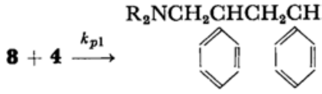


(**8**) (3)

The resulting sodium salt **8** transmetalates with the amine **6** to produce the compound **1** and at the same time reacts with styrene (**4**).

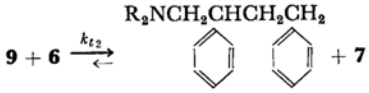


(**1**) (4)

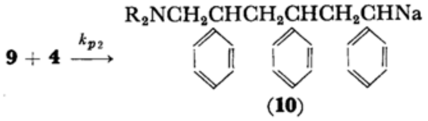


(**9**) (5)

The reactions (4) and (5) compete for the compound **8**. Both the chain transfer reaction (6) and the propagation reaction (7) take place also competitively for the compound **9**.

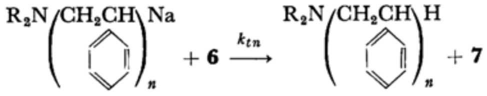


(**2**) (6)

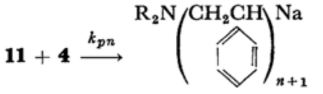


(**10**) (7)

Generally, the competitive reactions (8) and (9) take place for the organosodium compound **11**.

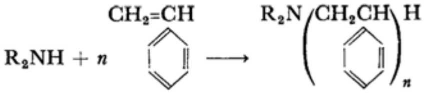


(**11**) (**12**) (8)



(**13**) (9)

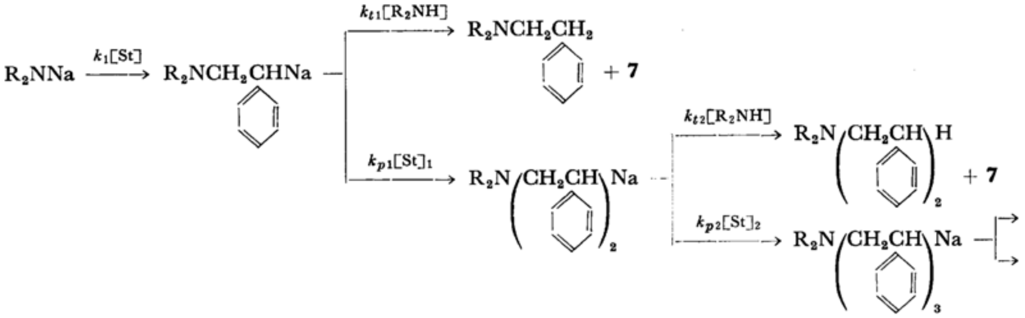
In the above equations, the notations k_i, k_{tn} and k_{pn} express the rate constants of the initiation reaction (3), the transfer reaction (8) and the propagation reaction (9), respectively. The reactions (3), (4), (5), (6), (7), (8) and (9) constitute a typical telomerization reaction. In fact, on combining Eqs. (3), (8) and (9) for $n=1, 2, \cdots, n-1$, the general equation of telomerization is obtained.



(10)

It may be understood from this reaction scheme that the telomers **1**, **2** and **3** are prepared by the anionic telomerization of styrene with the secondary amines.

Compositions of the Telomers. The reaction scheme proposed in the preceding section may be described as follows.

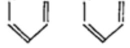
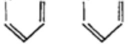
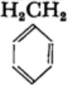
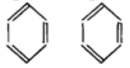
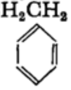
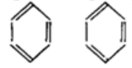


In the reaction styrene was added dropwise, and so the concentrations of styrene with which the organometallic compounds **7**, **8**, **9**, **10** and **11** reacted were different and were in the following order.

$$[\mathrm{St}] > [\mathrm{St}]_1 > [\mathrm{St}]_2 > [\mathrm{St}]_3 > \cdots \qquad (11)$$

If we suppose that the rate constants of the propagation reactions and the chain transfer reactions are approximately independent of n and the concentration of amine remains almost unchanged in a few minutes, the ratios of the rates of the transfer reactions to those of the propagation reactions

TABLE 4. CHARACTERIZATION OF THE TELOMERS

Molecular formula Structural formula			Elementary analysis		Molecular weight			Refractive index	Bp °C/mmHg
			Calcd %	Found %	Calcd	Mass	VPO		
$C_{12}H_{19}N$ $Et_2NCH_2CH_2$ 	(**1a**)	C H N	81.30 10.80 7.90	81.16 10.86 7.64	177.28	177	183	1.4972	77/0.1
$C_{20}H_{27}N$ $Et_2NCH_2CHCH_2CH_2$ 	(**2a**)	C H N	85.35 9.67 4.98	85.63 9.92 4.81	281.42	281	277	1.5367	136/0.1
$C_{28}H_{35}N$ $Et_2NCH_2CHCH_2CHCH_2CH_2$ 	(**3a**)	C H N	87.22 9.15 3.63	86.94 9.31 3.36	385.57	385	377	1.5576	212/0.1
$C_{14}H_{23}N$ $n\text{-}Pr_2NCH_2CH_2$ 	(**1b**)	C H N	81.89 11.29 6.82	81.86 11.36 7.00	205.33	205	202	1.4889	94/0.03
$C_{22}H_{31}N$ $n\text{-}Pr_2NCH_2CHCH_2CH_2$ 	(**2b**)	C H N	85.38 10.10 4.53	85.27 10.07 4.58	309.48	309	313	1.5257	155/0.03
$C_{30}H_{39}N$ $n\text{-}Pr_2NCH_2CHCH_2CHCH_2CH_2$ 	(**3a**)	C H N	87.11 9.50 3.39	87.04 9.07 3.05	413.62	···	408	1.5490	199/0.03
$C_{16}H_{27}N$ $n\text{-}Bu_2NCH_2CH_2$ 	(**1c**)	C H N	82.34 11.66 6.00	82.15 11.93 5.58	233.38	233	233	1.4990	148/4
$C_{24}H_{35}N$ $n\text{-}Bu_2NCH_2CHCH_2CH_2$ 	(**2c**)	C H N	85.40 10.45 4.15	85.89 10.04 4.20	337.53	338	334	1.5336	217/4
$C_{32}H_{43}N$ $n\text{-}Bu_2NCH_2CHCH_2CHCH_2CH_2$ 	(**3c**)	C H N	87.02 9.81 3.17	87.63 9.24 3.19	441.67	···	444	1.5565	232/0.02
$C_{16}H_{27}N$ $isoBu_2NCH_2CH_2$ 	(**1d**)	C H N	82.34 11.66 6.00	82.06 11.87 5.81	233.38	233	235	1.4883	130/4
$C_{24}H_{35}N$ $isoBu_2NCH_2CHCH_2CH_2$ 	(**2d**)	C H N	85.40 10.45 4.15	85.58 10.17 4.10	337.53	338	318	1.5221	202/4
$C_{32}H_{43}N$ $isoBu_2NCH_2CHCH_2CHCH_2CH_2$ 	(**2d**)	C H N	87.02 9.81 3.17	87.10 9.84 3.01	441.67	···	432	1.5403	194/0.04

give the following inequality.

$$\frac{k_{t1}[\mathrm{R_2NH}]}{k_{p1}[\mathrm{St}]_1} < \frac{k_{t2}[\mathrm{R_2NH}]}{k_{p2}[\mathrm{St}]_2} < \frac{k_{t3}[\mathrm{R_2NH}]}{k_{p3}[\mathrm{St}]_3} < \cdots \qquad (12)$$

Equation (12) shows that there may be a maximum in the yields of the telomers. The reactivities of the amines in the transfer reactions are supposed to be in the following order mainly because of the steric effects of the alkyl groups attached to nitrogen atoms.

$$k_{tn(\mathrm{Et_2NH})} > k_{tn(n\text{-}\mathrm{Pr_2NH})} > k_{tn(n\text{-}\mathrm{Bu_2NH})} > k_{tn(\mathrm{IsoBu_2NH})} \qquad (13)$$

The smaller the rate constants of the transfer reactions, the larger the average degrees of polymerization or the average degree of telomerization become. In this experiment only the telomers with $n=1$, 2 and 3 were separated, but some of the higher homologs of telomers are considered to have been formed and to have remained undistilled in residue. On controlling the ratio of styrene to the amine during the reaction, one can prepare the mixture of telomers with arbitrary average molecular weight in the region of oligomers.

Experimental

Physical Data. For mass spectral analysis, a Hitachi RMU-6D mass spectrometer was employed with the electron beam energy at 80 eV. The molecular weight determination by vapor pressure osmometry was carried out in benzene at 37°C on a Hewlett Packard Model 302 vapor pressure osmometer. IR spectra were recorded on a Hitachi Perkin-Elmer 125 grating infrared spectrophotometer. Proton NMR spectra were obtained on a Hitachi Model R-20 spectrophotometer using tetramethylsilane as an internal standard in carbon tetrachloride.

Materials. Styrene was dried over anhydrous magnesium sulfate for a day or more and was distilled under reduced pressure. Amines were dried over sodium hydroxide and were distilled under atmospheric or reduced pressure according to their boiling points.

General Procedure for Telomerization. In a four-necked round-bottomed flask, provided with a mechanical stirrer, a reflux condenser, a dropping funnel and an inlet of nitrogen, are placed a secondary amine and finely sliced sodium. The flask was heated to a prescribed temperature in an oil bath. The oil was agitated mechanically and its temperature was controlled by a thermostat. Styrene was added dropwise to the amine in 0.3 to 1.3 hr, and thereafter the mixture was kept standing for reaction for further 3 hr. Then the solution was cooled to room temperature and the alkali was decomposed by adding an equivalent amount of methanol and was neutralized by a 0.1 N hydrochloric acid. A small amount of benzene was added to this reaction mixture, if necessary, in order to make the solution uniform and the resulting solution was washed with water, dried and distilled *in vacuo*.

Diethyl-2-phenylethylamine (1a), Diethyl-2,4-diphenylbutylamine (2a) and Diethyl-2,4,6-triphenylhexylamine (3a). To 21.1 g of diethylamine and 0.7 g of sodium which were heated to 50.0±0.5°C, 62.3 g of styrene was added dropwise during 0.5 hr and the reaction took place for a further 3 hr. To the reaction mixture that was cooled to room temperature were added 3.1 m*l* of methanol and 10.0 m*l* of water. Then the solution was neutralized with 0.1 N hydrochloric acid, washed with 50 m*l* of water, and the organic layer was separated, dried and distilled *in vacuo* to give 42.2 g (39.67%) of the telomer **1a** at 77°C/4 mmHg, 5.78 g (6.84%) of the telomer **2a** at 136°C/4 mmHg and 4.74 g (6.18%) of the telomer **3a** at 212°C/0.02 mmHg. The other telomers were obtained in similar procedures.