prepared in ether and added to a tetrahydrofuran solution of the compound being metalated.

In a typical reaction, to a 50-ml. tetrahydrofuran solution of 8.0 g. (0.035 mole) of dibenzothiophene was added 28 ml. of ether in order to attain a final ether-tetrahydrofuran ratio of 6:5. To this solution was added 33 ml. of a 1.23*M* *n*-butyllithium solution in ether. The addition was carried out using an ice bath during 15 min. After the reaction mixture had stirred at room temperature for 5 hr., it was carbonated and hydrolyzed. Work-up of the water layer resulted in the isolation of 8.8 g. of crude 4-dibenzothiophenecarboxylic acid. Recrystallization from glacial acetic acid gave 5.9 g. (60%) of the acid melting at 261–264°.

Dibenzofuran, dibenzothiophene and *N*-ethylcarbazole were metalated with methyl-, *n*-butyl- and phenyllithium in the mixed ether-tetrahydrofuran solvent using the conditions shown in Table I.

Metalations in tetrahydrofuran. (*a*) *Phenyllithium.* Phenyllithium was prepared in tetrahydrofuran in yields of 81–82% according to a published procedure.[13] After the addition of the phenyl bromide was completed, the mixture was stirred at −60° for 1–2 hr., allowed to warm up to −35°, and then decanted into a jacketed addition funnel previously cooled to −20°.

In a typical reaction, to a 50-ml. tetrahydrofuran solution of 6.8 g. (0.035 mole) of *N*-ethylcarbazole cooled by an ice bath was added 55 ml. of a 0.68*M* phenyllithium solution in tetrahydrofuran during 20 min. The reaction mixture was stirred at room temperature for 5 hr., then carbonated and hydrolyzed.

The water layer was boiled to remove any dissolved solvent, acidified with concentrated hydrochloric acid, and filtered hot. A crude yield of 19% of 9-ethylcarbazole-1-carboxylic acid was obtained. Recrystallization from carbon tetrachloride resulted in 9.6% of the acid melting at 163–165°.

Dibenzofuran and dibenzothiophene were also metalated with phenyllithium in tetrahydrofuran as indicated in Table I.

(*b*) *Methyllithium.* The three heterocycles were metalated with methyllithium in tetrahydrofuran using the conditions given in Table I. Methyllithium was prepared in tetrahydrofuran by bubbling methyl chloride gas through a tetrahydrofuran suspension of an excess of lithium wire.[13]

(*c*) *n-Butyllithium.* The metalations of dibenzofuran, dibenzothiophene and *N*-ethylcarbazole were carried out with *n*-butyllithium in tetrahydrofuran. The results of these reactions are shown in Table I. The preparation of *n*-butyllithium in tetrahydrofuran was carried out according to a published procedure.[13]

Metalation of naphthalene with n-butyllithium. Run I. To a 100-ml. tetrahydrofuran solution of 12.8 g. (0.1 mole) of naphthalene was added 182 ml. of a 1.34*M* *n*-butyllithium solution in ether. The addition was carried out at 0° over a period of 45 min. The reaction mixture was stirred at room temperature for 16 hr., carbonated, and hydrolyzed. From the acidified water layer was isolated 4.3 g. (25%) of a mixture of α- and β-naphthoic acids. The crude acid was dissolved in ammonium hydroxide and a 5% solution of calcium chloride added to precipitate the calcium salt of the β-naphthoic acid. Filtration and acidification gave 1.0 g. (5.8%) of material which melted over the range 165–180°. Upon recrystallization from aqueous acetic acid there was obtained 0.76 g. (4.4%) of β-naphthoic acid melting at 178–182°. A mixture of this material with an authentic sample (m.p. 184–185°) melted at 181–183°. The α-naphthoic acid obtained from the acidification of the filtrate from the β-isomer was found to contain a small amount of the β-naphthoic acid, therefore the calcium chloride procedure was repeated. The α-naphthoic acid was also recrystallized from aqueous acetic acid and yielded 8.2% of acid melting at 155–159°. A mixture of this material with an authentic sample (m.p. 158–160°) melted at 155–159°.

Run II. The preceding reaction was repeated extending the time of metalation to 36 hr. A crude yield of 38.2% of the mixture of acids was realized. As in the first experiment, a large amount of material was lost in the separation and purification procedure. The final yields were 8.9% α-naphthoic acid and 9.3% β-naphthoic acid.

Run III. A third run was made in which the reaction mixture was refluxed for 3 hr. The crude yield of the mixture of acids was 22.8%. Pure α-naphthoic acid was isolated in a yield of 6%, and pure β-naphthoic acid in a yield of 3%.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Copolymers of Anthracene with Styrene and *p*-Chlorostyrene[1]

C. S. MARVEL AND B. D. WILSON

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Anthracene has been copolymerized with styrene and *p*-chlorostyrene, and 2-chloroanthracene has been copolymerized with styrene. Anthracene could not be copolymerized with acrylonitrile, methyl acrylate, or vinyl chloride.

Earlier work in this laboratory has shown that anthracene and butadiene can be copolymerized[2] and that the anthracene is incorporated in the polymer chain as a 9,10-dihydroanthracene derivative. In this communication are described successful copolymerizations of anthracene with styrene and *p*-chlorostyrene.

One difficulty in obtaining satisfactory incorporation of anthracene in the earlier copolymer resulted from its very low solubility in the comonomer and benzene was added to the system to in-

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(1) The work discussed herein was performed under contract AF-33(616)-3772 with the Materials Laboratory of Wright Air Development Center, Wright-Patterson Air Force Base, Ohio; Lt. L. E. Coleman and Lt. Paul D. Shaw, project engineers.

(2) C. S. Marvel and W. S. Anderson, *J. Am. Chem. Soc.*, **75**, 4600 (1953).

TABLE I

SOLUTION POLYMERIZATIONS

Polymer No.	Solvent	Solvent Vol., ml.	Initiator[a]	Initiator Wt., mg.	Anthracene, g.	Styrene, ml.	Hours Tumbled	Polymer Yield, g.	η (0.25% in benzene)
2	Iodobenzene	35	AIBN	51.4	—	15.0	10	0.9	0.482
4	Benzene	35	AIBN	51.7	—	15.0	10	0.7	0.347
7	Iodobenzene	35	$(\phi COO\text{-})_2$	45.1	—	15.0	19	1.1	0.734
8	Iodobenzene	35	$(\phi COO\text{-})_2$	44.5	—	15.0	19	1.1	0.731
10	Benzene	35	$(\phi COO\text{-})_2$	45.0	—	15.0	19	0.9	0.584
11	Benzene	35	$(\phi COO\text{-})_2$	45.0	—	15.0	19	0.8	0.586
14	Iodobenzene	50	$(\phi COO\text{-})_2$	19.5	1.55	1.00	24	[b]	—
16	Iodobenzene	60	AIBN	21.0	3.10	2.00	28	[b]	—
19	Benzene	60	AIBN	16.1	1.55	2.00	27	[b]	—
22	Benzene	60	AIBN	46.5	1.55	10.0	28	[b]	—

[a] AIBN = azobisisobutyronitrile, $(\phi COO\text{-})_2$ = benzoyl peroxide. [b] No polymer was obtained.

crease this solubility.[2] It has been shown[3] that iodobenzene is a much better solvent than benzene for anthracene. Hence some polymerization experiments with styrene were carried out in systems containing benzene and iodobenzene. These established the fact that there was apparently even less chain transfer action with iodobenzene than with benzene and therefore, in many of the further experiments with anthracene, iodobenzene was selected as a blending agent.

It is a bit surprising that anthracene can be incorporated into a vinyl-type polymer by free radical initiated reactions since there is considerable evidence that anthracene is a trap for radicals. For example, Batten[4] has demonstrated that radical chain decomposition of benzoyl peroxide is almost completely inhibited by anthracene. It was found that copolymerization of styrene and anthracene apparently proceeds slower than the homopolymerization of styrene. It was also shown that a lower molecular weight copolymer was obtained with styrene and anthracene when the oil soluble initiator, azobisisobutyronitrile, was used than when initiation was produced in the water phase of the emulsion by use of potassium persulfate. This evident effect of the location of the initiation reaction is also confirmed by the fact that solution copolymerization experiments with styrene and anthracene produced no polymer.

In typical emulsion systems with added solvent,[2] styrene and anthracene did copolymerize. The percentage incorporation of anthracene was determined by ultraviolet spectrophotometry using 9,10-dimethyl-9,10-dihydroanthracene[2] as a model compound for the incorporated dihydroanthracene unit and ethylbenzene[5] for the incorporated sytrene unit. Both cyclohexane and tetrahydrofuran were used as polymer solvents in determining the ultraviolet absorption. The results were acceptable in either solvent but the tetrahydrofuran seemed in general the more satisfactory solvent. It was necessary to use solutions of approximately the same concentrations in the unknown and known materials in order to make comparisons of analytical accuracy since the polymer solutions did not appear to obey Beer's law. It has also been shown by Pestemer and Gübitz[6] that the effect of the length of the alkyl group on the ultraviolet spectrum of an alkyl substituted aromatic nucleus is to have a small and diminishing bathochromic shift with each additional CH_2 group. Anderson[7] found that there was an error of about 1 mμ in using 9,10-dimethyl-9,10-dihydroanthracene as a model compound in the anthracene-butadiene copolymers. In the present work with styrene copolymers, it was found that there was a very steep slope to the absorption curve near the maxima and minima used for the calculations, and thus a 1 mμ error in wave length would produce a considerable error in absorbance. These and other more minor possible sources of error make it necessary to accept the composition of the styrene-anthracene copolymer as approximate.

To get another method of checking composition, by use of direct analysis, *p*-chlorostyrene was used as a comonomer in place of styrene. The results with *p*-chlorostyrene were confirmatory of those obtained with styrene.

The copolymers of styrene and *p*-chlorostyrene with anthracene have not shown any interesting new properties in a preliminary study. For example, their thermal stabilities are lower than the stabilities of the corresponding homopolymers, which might be expected for a polymer with only a minor amount of a second monomer randomly incorporated in the polymer chain. It is doubtful if copolymers with a much higher content of anthra-

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(3) G. R. Somayajuki and S. R. Palit, *J. Phys. Chem.*, **58**, 417 (1954).

(4) J. J. Batten, *J. Chem. Soc.*, 4687 (1956).

(5) H. B. Klevens, *J. Polymer Sci.*, **10**, 97 (1953).

(6) M. Pestemer and O. Gübitz, *Monatsh.*, **64**, 426 (1934).

(7) W. S. Anderson, Ph.D. thesis, University of Illinois, 1954.

TABLE II

EMULSION POLYMERIZATIONS[a]

Polymer No.	Emulsifier Soln., ml.	Initiator Soln., ml.	Anthracene, g.	Comonomer	Vol. of Comonomer, ml.	Oil phase Solvent	Solvent Volume, ml.	Modifier, mg.	Hours Tumbled	η (0.25% in benzene)
26	35	2.0	1.00	Styrene	20.0	Benzene	10.0	60	21	0.48
27	35	2.0	1.00	Styrene	20.0	Benzene	10.0	15	91	1.15
28	35	2.0	1.00	Styrene	20.0	Benzene	10.0	15	91	1.40
29	35	2.0	1.00	*p*-Chlorostyrene	20.0	Benzene	10.0	15	96	0.727
30	35	2.0	2.00	*p*-Chlorostyrene	20.0	Iodobenzene	10.0	15	96	0.754
31	35	1.0	1.00	*p*-Chlorostyrene	5.0	[b]	20	15	100	0.364
32	35	[c]	1.00	*p*-Chlorostyrene	5.0	[b]	20	15	100	0.283
33	28	1.5	1.50	*p*-Chlorostyrene	15.0	Iodobenzene	7.5	15	20	0.815
34	35	2.0	1.00	Acrylonitrile	20.0	Benzene	10.0	15	84	[d]
35	35	2.0	—	Acrylonitrile	20.0	Benzene	10.0	15	84	[e]
36	35	2.0	1.00	Vinyl chloride	(19.0 g.)	Benzene	10.0	30	101	[d]
37	35	2.0	—	Vinyl chloride	(19.0 g.)	Benzene	10.0	30	101	[e]
38	35	2.0	1.00	Methyl acrylate	20.0	Benzene	10.0	30	102	[d]
39	35	2.0	—	Methyl acrylate	20.0	Benzene	10.0	30	102	[e]
40	20	2.0	—	*p*-Chlorostyrene	10.0	Benzene	5.0	15	18	0.620
42	28	1.5	1.00[f]	Styrene	15.0	Iodobenzene	7.5	15	36	1.70
43	28	1.5	2.00[f]	Styrene	15.0	Iodobenzene	7.5	15	20	1.67

[a] The conversion in all cases where polymer was formed was slightly over 100%, uncorrected for inclusion of the recipe ingredients. [b] A mixture of 19% benzene and 81% iodobenzene by volume was used. [c] The initiator was 30 mg. of azo-bis-isobutyronitrile. [d] No polymer was formed. [e] A good homopolymer was obtained, but not characterized. [f] 2-Chloroanthracene was used in place of anthracene.

TABLE III

ANTHRACENE CONTENT OF ANTHRACENE-STYRENE COPOLYMERS (CYCLOHEXANE SOLUTIONS)

Polymer No.	Prepared[a] Conc. (g./l.)	Av. Calcd. Conc. from UV Data (g./l.)			% Deviation in Total Polymer Conc.	Av. Wt. % Anthracene in Polymer
		Styrene	Anthracene	Total		
26	0.349	0.340	0.0469	0.387	10.3	12.1
27	0.150	0.171	0.0210	0.192	24.6	10.9
28	0.107	0.119	0.0151	0.134	22.3	11.3

[a] These were saturated solutions of polymer in cyclohexane.

TABLE IV

ANTHRACENE CONTENT OF ANTHRACENE-STYRENE COPOLYMERS (TETRAHYDROFURAN SOLUTIONS)

Polymer No.	Prepared Conc. (g./l.)	Av. Calcd. Conc. from UV Data (g./l.)			% Deviation in Total Polymer Conc.	Av. Wt. % Anthracene in Polymer
		Styrene	Anthracene	Total		
26	0.479	0.385	0.0521	0.437	9.17	11.9
27	0.445	0.348^{+}	0.0504	0.399	10.9	12.6
28	0.450	0.389^{-}	0.0444	0.433	3.84	10.2

TABLE V

ANTHRACENE CONTENT OF ANTHRACENE-*p*-CHLOROSTYRENE COPOLYMERS

Polymer No.	Elemental Analysis				Calculated Anthracene Content (Wt. %)		
	% C (av.)	% H (av.)	Cl	Total	C analysis	Cl analysis	Average
29	70.26	5.34	24.57	100.17	3.7	3.94	3.8
30	70.51	5.42	24.23	100.16	4.72	5.27	5.0
31	71.01	5.54	23.22	99.77	6.72	9.22	8
32	71.24	5.41	23.48	100.13	7.64	8.20	7.9
33	70.13	5.45	24.38	99.96	3.2	4.69	4
p-Chloro-styrene	69.33	5.09	25.58	100.00			
Anthracene	94.34	5.66	—	100.00			

TABLE VI

2-CHLOROANTHRACENE CONTENT OF 2-CHLOROANTHRACENE-STYRENE COPOLYMERS

Polymer No.	Elemental Analysis				Calculated 2-Chloroanthracene Content (Wt. %)			
	% C (av.)	% H (av.)	Cl	Total	C anal.	H anal.	Cl anal.	Av.
42	91.11	7.53	1.35	99.99	8.71	6.1[a]	8.10	8.4
43	90.98	7.48	1.38	99.84	9.70	7.5	8.28	8.5
2-Chloro-styrene	79.06	4.27	16.67	100.00				
Styrene	92.26	7.74	—	100.00				

[a] This value was not used in calculating the average.

TABLE VII

THERMAL STABILITIES OF SELECTED POLYMERS IN A NITROGEN ATMOSPHERE

Polymer No.	Sample Wt., mg.	% Wt. Loss in 4 Hr.
7	204.1	6.27 at 290°
[a]	120.3	8.56 at 285°
42	196.9	13.1 at 300°
40	199.5	5.11 at 305°
29	204.6	10.5 at 305°
31	200.4	5.49 at 290°

[a] Approximately a 1:1 mixture of numbers 27 and 28 was used.

cene units can be prepared due to solubility problems and to the inhibiting effect of anthracene.

No copolymers of anthracene could be prepared with acrylonitrile, methyl acrylate, or vinyl chloride in emulsion systems. The anthracene acted as a polymerization inhibitor in these cases.

2-Chloroanthracene and styrene also copolymerize readily in emulsion systems and a few examples of this are included in the experimental part of this paper.

EXPERIMENTAL

Solution polymerizations. These polymerizations were conducted in 4-oz. screw-cap bottles sealed with acrylonitrile rubber gaskets. The charges are given in Table I. The bottles were tumbled end-over-end at 29 r.p.m. for the specified period in a constant temperature bath at 50 ± 1°. The polymers were isolated by pouring into a large volume of stirred methanol followed by drying under vacuum. The polymers were purified by a twofold precipitation from benzene solution into methanol.

Emulsion polymerizations. These polymerizations were conducted in 4-oz. screw-cap bottles sealed with acrylonitrile rubber gaskets. The charges are given in Table II. The emulsifier solution was a 2.86% aqueous solution of Office of Rubber Research soap (specification L.M. 2.3.0.5.2). The initiator solution was a 3.0% aqueous solution of potassium persulfate. The modifier was technical lauryl mercaptan (Hooker Electrochemical Co.). The bottles were tumbled end-over-end at 29 r.p.m. for the specified period in a constant temperature bath at 50 ± 1°. The polymers were isolated by addition of 5 ml. of a 4.2% aqueous solution of sulfuric acid saturated with sodium chloride after first protecting against air oxidation by the addition of 5 ml. of a saturated methanol solution of *N*-phenyl-β-naphthylamine. The polymers were purified by washing well with water, drying, and repeated precipitation (7 to 10 times) from benzene solution into methanol. All samples were completely soluble and showed no signs of crosslinking. The ultraviolet absorption spectra were obtained with a Cary recording spectrophotometer, Model 11, using solutions in tetrahydrofuran or saturated solutions in cyclohexane. The tetrahydrofuran was purified by passage through a column of Linde Molecular Sieves, type 13X. The cyclohexane was Eastman Kodak spectro grade, used directly.

The thermal stabilities were obtained by means of a homemade thermobalance similar to that described by Winslow and Matreyek.[8]

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(8) F. H. Winslow and W. Matreyek, *J. Polymer Sci.*, **22**, 315 (1956).