[Contribution from the Noyes Chemical Laboratory, University of Illinois]

COPOLYMERIZATIONS OF CONJUGATED UNSATURATED CARBONYL SYSTEMS CONTAINING THIOPHENE UNITS

C. S. MARVEL, JAMES M. QUINN, and JOHN S. SHOWELL

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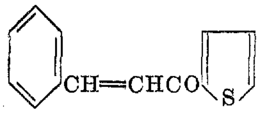
It has recently been established that α,β-unsaturated carbonyl compounds of the type $C_6H_5CH{=}CHCOX$ copolymerize readily with a considerable variety of vinyl and diene monomers (1, 2). In addition it has been found that several furan derivatives of this type will copolymerize with dienes and styrene (1). The present investigation deals with thiophene analogs of this class of compounds.

The thiophene derivatives which have been studied are the following.



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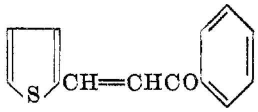

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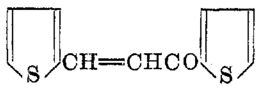

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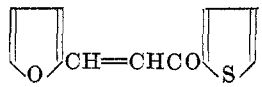

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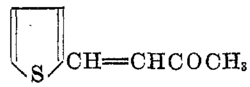

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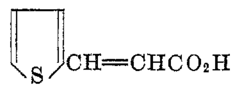

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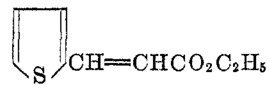

VII

All of these neutral molecules were copolymerized with 1,3-butadiene in the Mutual recipe (3). The acidic monomer (VI) was not tried in the alkaline recipe but it did copolymerize with butadiene in an acid side azobisisobutyronitrile-initiated recipe. Benzal-2-acetothienone (I) was also copolymerized with butadiene in a modified Mutual recipe initiated with azobisisobutyronitrile (4), in a cumene hydroperoxide recipe (4), and in a Nitrazole CF recipe (5). Also 2-thenal-2′-acetothienone (III) copolymerized with butadiene in the cumene hydroperoxide-initiated system (4). It, therefore, seems probable that the other monomers of this group can be used in recipes other than the Mutual. Since no differences were noted in the copolymers of butadiene and the two thiophene monomers (II and III) prepared in the different recipes, the other combinations were studied only in the Mutual recipe.

These thiophene-containing monomers were less readily copolymerized with butadiene than was the case with the corresponding monomers with phenyl in place of the thienyl group (1, 2). Much more careful purification of the thiophene-containing monomer was required in order to get copolymerization reaction to take place. The copolymerizations usually required a longer time at 50° and gave lower conversions of low viscosity polymers than did the corresponding phenyl compounds.

Of the butadiene copolymers only the one with 10 parts of 2-thenalacetophenone (II) in the charging stock, prepared in the Mutual recipe, was deemed to have sufficiently good solubility and viscosity to justify evaluation as a rubber. This copolymer was compounded, vulcanized, and evaluated by standard A.S.T.M. procedure for stress-strain properties (6), low temperature flexibility (7), hysteresis (8), and oil resistance (9). The stress-strain properties

TABLE I

Copolymerization Experiments With Various Vinyl Monomers

Thiophene derivative	Comonomer								
	Butadiene	Isoprene	Acrylonitrile	Methyl acrylate	Methyl methacrylate	Methyl vinyl ketone	Styrene	Vinyl acetate	Ethyl acrylate
Benzal-2-acetothienone	+	+	+(?)	+	+	+	+	−	−
2-Thenalacetophenone	+	+	+	−	−	+	+	−	−
2-Thenal-2′-acetothienone	+	+	−	−	−	+	+	−	−
2-Thenalacetone	+	−	+	−	−	−	−	−	−
Ethyl β-(2-thienyl)acrylate	+	+	−	−	+	−	+	−	−
β-(2-Thienyl)acrylic acid	+	+	+		+		+	−	−

were about like standard GR-S (50°), the Gehman low temperature properties were good, and the oil resistance was slightly better than GR-S control. The hysteresis properties were not as good as for a GR-S control.

A number of copolymerization experiments with these monomers and such monomers as isoprene, acrylonitrile, methyl and ethyl acrylates, methyl methacrylate, styrene, methyl vinyl ketone, and vinyl acetate were tried in emulsion and in bulk recipes. No one of the thiophene-containing monomers could be copolymerized with vinyl acetate or ethyl acrylate under any conditions which were tried. All except 2-thenalacetone copolymerized with isoprene. All except 2-thenal-2′-acetothienone and ethyl β-(2-thienyl)acrylate copolymerized with acrylonitrile but the conversions were very low even at long times. The copolymerization experiments are briefly summarized in Table I and the details are recorded in the experimental part. That copolymerization had occurred in these cases listed as positive was demonstrated by the infrared spectrum of each copolymer which showed absorption at the expected places for the functional groups which should be present.

None of these thiophene derivatives could be homopolymerized under any conditions which we tried which included standard procedure for bulk, solution,

TABLE II

Copolymers of Some Thienylated α,β-Unsaturated Carbonyl Compounds With Various Monomers

Monomer	Comonomer	Charge ratio[a]	Recipe[b]	Modifier, g.	Time, Hrs.	Conversion, %	Solubility, %	Inherent viscosity	Appearance of polymer	Softening point, °C.	Groups indicated by infrared analysis
Benzal-2-acetothienone	Acrylonitrile	20/80	M	0.059	24	0.1	—	—	White powder	—	Unconjugated ketone carbonyl (1710 cm^{-1}), phenyl (1600, 1580 cm^{-1})[c]
Benzal-2-acetothienone	Isoprene	10/90	M	.059	26	80.0	66.9	1.54	White elastomer	55–95	Ketone carbonyl conjugated with thiophene ring (1736, 1715, 1654 cm^{-1}), phenyl (1599, 1580 cm^{-1})
Benzal-2-acetothienone	Methyl acrylate	9.5/90.5	B	—	43	100	100	0.44	Tough, clear	95–120	Ester carbonyl (1730 cm^{-1}), ketone carbonyl conjugated with thiophene ring (1654 cm^{-1}), phenyl (1599, 1580 cm^{-1})
Benzal-2-acetothienone	Methyl methacrylate	10/90	M	.059	26	100	90.2	1.85	White powder	>200	Ketone carbonyl conjugated with thiophene ring (1654 cm^{-1}), nonconjugated ester carbonyl (1728 cm^{-1}), phenyl (1599, 1580 cm^{-1})
2-Thenalacetophenone	Methyl vinyl ketone	8.2/91.8	M	.059	24	12.5	88.6	.03	Dark red sticky solid[f]	40–45	Ketone carbonyl (1649, 1715 cm^{-1}), phenyl (1578, 1595, 1515, 698 cm^{-1}), thienyl (690, 720, 725 cm^{-1})
2-Thenalacetophenone	Styrene	5/95	B	—	28	6.8	100	.15	Hard, crumbly white solid	108–119	Ketone carbonyl (1673 cm^{-1}), phenyl (698, 757, 724, 1493, 1602 cm^{-1})
2-Thenal-2′-acetothienone	Isoprene	10/90	M	.059	26	35.0	86.2	.66	Tacky, white	—	Unconjugated ketone carbonyl (1712 cm^{-1}), ketone carbonyl conjugated with thienyl (1650 cm^{-1}), thienyl (1588 cm^{-1})
2-Thenal-2′-acetothienone	Methyl vinyl ketone	10.5/89.5	M	.059	24	20.0	91.2	.40	Yellow, sticky solid	—	Unconjugated ketone carbonyl (1710 cm^{-1}), ketone carbonyl conjugated with thienyl (1666 cm^{-1})
2-Thenal-2′-acetothienone	Styrene	10/90	B	—	28	2.8	96.7	.01	Yellow crystalline solid	94–123	Ketone carbonyl conjugated with thienyl (1648 cm^{-1}), phenyl (1585, 1600 cm^{-1})

Benzal-2-acetothienone	Methyl vinyl ketone	8.2/91.8	M	.059	24	40.0	35.8	.19	Tough, white	60–130	Ketone carbonyl conjugated with thiophene ring (1654 cm^{-1}), phenyl (1597, 1580 cm^{-1})
Benzal-2-acetothienone	Styrene	10/90	B	—	28	40.0	82.0	.30	Tough, clear, yellowish	120–130	Ketone carbonyl conjugated with thiophene ring (1654 cm^{-1}), phenyl (1600, 1580 cm^{-1})
2-Thenalacetophenone	Acrylonitrile	10/90	M	.012	24	4.5	—	—	Tan powder[d]	>200	Ketone carbonyl (1715 cm^{-1})
2-Thenalacetophenone	Isoprene	10/90	M	.059	44	100	65.3	2.05	Tacky white elastomer	90–130	Ketone carbonyl (1678 cm^{-1})
		10/90	M	.071	25.5	60.0	100	.91			
2-Thenalacetophenone	Methyl methacrylate	10/90	M	.059	24	3.0	96.4	.60	White powder[e]	>200	No thienyl, trace of phenyl (1598 cm^{-1}) and ketone carbonyl (1660 cm^{-1})
2-Thenalacetone	Acrylonitrile	10/90	M	.012	24	2.9	50.2	.02	Tan powder	—	—
Ethyl β-(2-thienyl) acrylate	Acrylonitrile	10/90	M	.0118	24	0.4	—	—	Tan powder	—	—
Ethyl β-(2-thienyl)acrylate	Isoprene	10/90	M	.059	26	100	47.8	1.08	Tacky, white	110–149	Thienyl (1602 cm^{-1}) ester carbonyl (1736 cm^{-1})
Ethyl β-(2-thienyl)acrylate	Methyl methacrylate	10/90	M	.059	24	68.9	100	.44	White powder	157–200	Thienyl (1602 cm^{-1}), ester carbonyl (1728 cm^{-1})
Ethyl β-(2-thienyl)acrylate	Styrene	10/90	B	—	28	6.02	100	.07	White powder	110–125	Thienyl (1602 cm^{-1}), phenyl (1588 cm^{-1}), ester carbonyl (1720 cm^{-1})
β-(2-Thienyl)acrylic acid	Acrylonitrile	10/90	A	.0118	24	2.95	1.8	.01	White powder	>200	—
β-(2-Thienyl)acrylic acid	Isoprene	5/95	A	.059	27	76.1	89.3	1.24	White elastomer	100–180	Thienyl (1602 cm^{-1}), acid carbonyl (1714 cm^{-1})
β-(2-Thienyl)acrylic acid	Methyl methacrylate	5/95	A	.059	28	41.1	93.8	.25	White powder	121–165	Thienyl (1602 cm^{-1}), ester carbonyl (1728 cm^{-1}), acid hydroxyl (3390 cm^{-1})
β-(2-Thienyl)acrylic acid	Styrene	5/95	B	—	28	10.9	92.5	.08	White powder	130–137	Acid carbonyl (1710 cm^{-1}), thienyl (1602 cm^{-1}), probably phenyl (1816 cm^{-1})

[a] Monomer/comonomer. [b] M = mutual; B = azobisisobutyronitrile-initiated bulk; A = azobisisobutyronitrile-initiated acid-side emulsion. All run at 50°. [c] The usual 1654 cm^{-1} band characteristic of ketone carbonyl conjugated with thiophene ring was absent. [d] Per cent sulfur in copolymer 2.24; per cent monomer in copolymer 16.7. [e] Per cent sulfur in copolymer 0.66; per cent monomer in copolymer 4.4. [f] Per cent sulfur in copolymer 7.28; per cent monomer in copolymer 48.7.

and emulsion polymerizations. No copolymerizations with butadiene were carried out under conditions which are favorable for determining reactivity ratios (7) for the monomers but the compositions of the copolymers as compared to the charging ratios are of interest in pointing out the trends toward alternation of monomer units. In every case examined at conversions of less than 70%, the copolymer was richer in the thiophene monomer than was the charging stock. At low conversion the increase was very marked. It therefore seems likely that there is a close approach to alternation of monomer units in the early stage of the copolymerization. Work designed to give this information is under way in this laboratory.

EXPERIMENTAL

PREPARATION OF MONOMERS

Benzal-2-acetothienone. Benzal-2-acetothienone was prepared by the reaction suggested by Brunswig (10) who gave no details on conditions of the reaction or analysis of his product. 2-Acetothienone, 116.2 g. (0.92 mole), was mixed with 97.6 g. (0.92 mole) of benzaldehyde in a 300-ml. round-bottomed flask, and anhydrous hydrogen chloride was passed through the mixture for three hours at 30°. The reaction mixture was then extracted with 1500 ml. of hexane (Skellysolve B). Concentration of the extract to about one-tenth of its original volume, followed by cooling to 0°, caused separation of crystals which were collected, dried, and recrystallized once from hexane (Skellysolve B) and twice from methanol to yield 135.5 g. (61.0%) of white crystals, m.p. 83.6–84.0°.

Anal. Calc'd for $C_{13}H_{10}OS$: C, 72.85; H, 4.71; S, 14.95.

Found: C, 72.96; H, 4.78; S, 15.00.

Ethyl β-(2-thienyl)acrylate. This ester was prepared by the method of King and Nord (11). The fraction boiling at 151–154° at 22 mm., n_D^{20} 1.5831, was collected in 36.7% yield.

2-Furfural-2′-acetothienone. This ketone was prepared by the reaction used by Weygand and Strobelt (12). To a solution of 100 g. of potassium hydroxide in 100 ml. of water and 379 ml. of methanol were added 155.7 g. (1.23 moles) of 2-acetothienone and 118.3 g. (1.23 moles) of furfural. This mixture was stirred for ten hours while the temperature was maintained at below 10°. The reaction mixture was then cooled to 0°, and the yellow crystals which precipitated were separated and dried at room temperature under reduced pressure. After two recrystallizations from hexane (Skellysolve B) and one from methanol 191.3 g. (76.2%) of 2-furfural-2′-acetothienone was obtained as yellow crystals, m.p. 70.8–71.6°.

2-Thenalacetone. This ketone was prepared by a method analogous to that used for the preparation of benzalacetone (13), substituting for benzaldehyde an equivalent amount of redistilled 2-thiophenealdehyde. The yield of redistilled product was 69%, boiling at 151–153° at 14 mm., n_D^{20} 1.6367.

2-Thenalacetophenone. This ketone was prepared by a modification of the method given in *Organic Syntheses* (14) for the preparation of benzalacetophenone. After three recrystallizations from 1½ times its weight of 95% ethanol, the light-yellow crystalline product was obtained in 84.4% yield; m.p. 58.4–59.2°.

2-Thenal-2′-acetothienone. This ketone was prepared according to the reaction reported by Weygand and Strobelt (12), who gave few details on this preparation. To a mixture of 100 g. of potassium hydroxide in 100 ml. of water and 379 ml. of methanol were added 144 g. (1.25 moles) of 2-thiophenealdehyde and 163.4 g. (1.25 moles) of 2-acetothienone. The mixture was stirred for 23 hours at 0°, giving rise to brown granules, which were collected and dried at room temperature under reduced pressure. The crude product was recrystallized first from a methanol-petroleum ether mixture and then twice more from methanol to yield 194.5 g. (71%) of yellow crystals; m.p. 99.2–99.8°.

Anal. Calc'd for $C_{11}H_{8}OS_2$: C, 60.00; H, 3.66; S, 29.10.

Found: C, 59.68; H, 3.63; S, 29.27.

β-(2-Thienyl)acrylic acid. This acid was prepared by the method of King and Nord (11). After two recrystallizations from 95% ethanol the product was obtained in 57.2% yield; m.p. 145–146°.

Commercial samples of acrylonitrile, ethyl acrylate, isoprene, maleic anhydride, methyl acrylate, methyl methacrylate, methyl vinyl ketone, styrene, and vinyl acetate were used in this study, and all were redistilled before use.

TABLE III

COMBINATIONS OF MONOMERS WHICH DID NOT YIELD COPOLYMERS

MONOMER	COMONOMER	CHARGE RATIO[a]	RECIPE[b]	MODIFIER, g.	TIME, Hrs.
Benzal-2-acetothienone	Ethyl acrylate	10/90	B	—	30
Benzal-2-acetothienone	Vinyl acetate	10/90	M	0.059	24
2-Thenalacetophenone	Ethyl acrylate	5/95	B	—	28
2-Thenalacetophenone	Maleic anhydride	10/90	B[c]	—	24
2-Thenalacetophenone	Methyl acrylate	5/95	B	—	28
2-Thenalacetophenone	Vinyl acetate	5/95	M	.071	18
2-Thenal-2′-acetothienone	Acrylonitrile	10/90	M	.012	24
2-Thenal-2′-acetothienone	Ethyl acrylate	10/90	B	—	30
2-Thenal-2′-acetothienone	Methyl acrylate	9.5/90.5	B	—	43
2-Thenal-2′-acetothienone	Methyl methacrylate	10/90	M	.059	24
2-Thenal-2′-acetothienone	Vinyl acetate	10/90	M	.059	24
2-Thenalacetone	Ethyl acrylate	10/90	B	—	30
2-Thenalacetone	Isoprene	15.4/84.6	M	.059	26
2-Thenalacetone	Methyl acrylate	10/90	B	—	43
2-Thenalacetone	Methyl methacrylate	10/90	M	.059	24
2-Thenalacetone	Methyl vinyl ketone	13.2/86.8	M	.059	24
2-Thenalacetone	Styrene	10/90	B	—	28
2-Thenalacetone	Vinyl acetate	10/90	M	.059	24
Ethyl β-(2-thienyl)acrylate	Ethyl acrylate	10/90	B	—	28
Ethyl β-(2-thienyl)acrylate	Methyl acrylate	10/90	B	—	28
Ethyl β-(2-thienyl)acrylate	Methyl vinyl ketone	32.3/67.7	M	.059	24
Ethyl β-(2-thienyl)acrylate	Vinyl acetate	10/90	M	.059	24
β-(2-Thienyl)acrylic acid	Ethyl acrylate	5/95	B	—	28
β-(2-Thienyl)acrylic acid	Vinyl acetate	10/90	B	—	28

[a] Monomer/comonomer.

[b] M = mutual; B = azobisisobutyronitrile-initiated bulk.

[c] Temperature 70°.

POLYMERIZATION RECIPES AND TECHNIQUES

GR-S Mutual recipe. The recipe of Frank and coworkers (3), adapted to a monomers charge of 20 g., was used in this study. Hooker's lauryl mercaptan (a mixture of primary mercaptans having the average molecular formula $C_{12.6}H_{26.2}SH$) was used as modifier. In some experiments azobisisobutyronitrile was substituted for potassium persulfate as initiator.

Cumene hydroperoxide recipe. A slight modification (1) of the recipe of Troyan and Tucker (4) was used in this work.

Nitrazole CF recipe. This recipe is that recently reported by Willis, Alliger, Johnson, and Otto (1, 5).

Acid-side recipe with azobisisobutyronitrile (15).

TABLE IV

COPOLYMERS OF BUTADIENE AND CONJUGATED UNSATURATED CARBONYL SYSTEMS CONTAINING THIOPHENE UNITS

NO.	MONOMER	CHARGE RATIO[a]	RECIPE[b]	MODIFIER, g.	INITIATOR, g.	TIME, Hrs.	CONVERSION, %	SOLUBILITY, %	INHERENT VISCOSITY	ANAL. S	% MONOMER INCORP., Found[c]
507	Benzal-2-acetothienone[d]	90/10	M	0.111	0.10	24	40.5	97.0	1.17	2.46	16.5
646	Benzal-2-acetothienone	90/10	M	.059	.10	27	44.0	92.0	2.00	—	—
404	Benzal-2-acetothienone	85/15	M	.084	.10	30	35.0	96.0	0.65	3.27	21.9
602	Benzal-2-acetothienone	85/15	M	.111	.10	30	41.5	97.4	1.40	—	—
606	Benzal-2-acetothienone	80/20	M	.056	.10	30	39.5	93.8	1.45	4.10	27.4
403	Benzal-2-acetothienone	90/10	MA	.084	.06	30	17.5	96.0	0.17	—	—
573	Benzal-2-acetothienone	90/10	N-CF	.042	.04	24	22.5	100.0	1.23	—	—
410	Benzal-2-acetothienone	90/10	CHP	.084	.04	30	20.5	78.0	0.15	—	—
739	Ethyl β-(2-thienyl)acrylate	90/10	M[e]	.047	.10	30	68.0	92.8	2.55	2.10	12.0
757	Ethyl β-(2-thienyl)acrylate	85/15	M	.047	.10	25	86.0	63.5	1.40	—	—
763	Ethyl β-(2-thienyl)acrylate	80/20	M	.047	.10	26	79.5	83.8	2.10	2.60	14.8
401	2-Furfural-2′-acetothienone	90/10	M	.084	.10	30	25.0	99.0	0.16	—	—
469	2-Furfural-2′-acetothienone	90/10	M	.084	.10	100	20.0	94.7	0.42	5.62	34.7
418	2-Furfural-2′-acetothienone	90/10	MA	.116	.06	50	21.5	90.0	0.04	—	—
419	2-Furfural-2′-acetothienone	90/10	CHP	.116	.04	48.5	15.0	88.0	0.06	—	—
269	2-Thenalacetone	95/5	M	.044	.10	19	27.0	100.0	1.03	2.27	10.8
371	2-Thenalacetone	90/10	M	.056	.10	43	40.5	93.5	1.56	4.30	20.4
381	2-Thenalacetone	80/20	M	.051	.10	90	54.5	97.7	1.71	6.38	30.2
382	2-Thenalacetone	80/20	M	.051	.10	93	54.0	93.0	1.60	6.46	30.6
327	2-Thenalacetophenone	95/5	M	.111	.10	17	52.0	100.0	1.73	1.23	8.2
362	2-Thenalacetophenone	90/10	MA	.111	.06	37	42.0	100.0	1.84	3.00	20.1
715	2-Thenalacetophenone	90/10	M[f]	.071	.10	26	63.0	94.8	1.66	2.12	14.2
389	2-Thenalacetophenone	85/15	M	.111	.10	35	55.0	84.4	1.88	4.07	27.2
654	2-Thenalacetophenone	80/20	M	.071	.10	30	42.0	94.7	1.10	—	—
409	2-Thenal-2′-acetothienone	90/10	M	.056	.10	72	54.0	73.0	1.02	5.20	17.9
474	2-Thenal-2′-acetothienone	85/15	M	.056	.10	100	42.0	82.8	0.73	10.57	36.4
513	2-Thenal-2′-acetothienone	90/10	MA	.111	.06	24	17.5	100.0	0.30	—	—
421	2-Thenal-2′-acetothienone	90/10	CHP	.084	.04	70	23.0	87.0	0.34	—	—
771	β-(2-Thienyl)acrylic acid	90/10	A	.071	.10	19	54.0	91.8	1.00	2.86	15.0
776	β-(2-Thienyl)acrylic acid	85/15	A	.071	.10	19	52.5	62.9	0.73	3.07	16.1
779	β-(2-Thienyl)acrylic acid	80/20	A	.071	.10	19	53.5	78.2	0.77	3.65	19.1

[a] Butadiene/comonomer. [b] M = Mutual; MA = Mutual, azobisisobutyronitrile-initiated; N-CF = Nitrazole-CF; CHP = Cumene hydroperoxide; A = Acid side recipe, azobisisobutyronitrile-initiated. [c] Per cent monomer incorporated in copolymer, as calculated from sulfur analysis. [d] Since three different molecular weight fractions (high, low, medium) had nearly identical sulfur content (2.16, 2.32, 2.32), it is concluded that this is a

Azobisisobutyronitrile	0.02–0.06 g.
MP-635-S*	2.00 ml.
Water (boiled and cooled under nitrogen to eliminate oxygen)	38.00 ml.
Hooker's lauryl mercaptan	0.025–0.100 g.
Monomers	20 g.

* The composition of this emulsifier is as follows:

Sodium alkanesulfonates in the C_{16} range	49.5%
Unreacted hydrocarbon	10.3%
Sodium chloride	0.86%
Sodium sulfate	0.4%

Balance, water and about 3% isopropyl alcohol.

Bulk recipe. The monomers were mixed and heated with azobisisobutyronitrile as the initiator.

Polymerizations. Polymerizations were conducted in 4-oz. polymerization bottles sealed with screw caps containing self-sealing rubber gaskets. Bottles were charged in the order listed in the recipes and then tumbled in a constant-temperature bath for the times noted in the tables. Temperature was 50°, unless otherwise noted.

Inherent viscosities (16). These were determined in Ostwald viscosimeters in benzene solution at 25°.

Table II summarizes the conditions under which polymers were formed with various comonomers, and certain of their properties, such as solubility, inherent viscosity, appearance and softening point. Characteristic groups incorporated in the copolymers are listed, such as carbonyl, phenyl, and thienyl, as determined by infrared analysis. Similarly Table IV summarizes data pertinent to butadiene copolymers.

Table III records the conditions under which a number of monomer-pairs failed to copolymerize.

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SUMMARY

α,β-Unsaturated carbonyl compounds containing thiophene groups have been studied in copolymerization reactions with a wide variety of monomers. In general it can be said that these substances copolymerize less readily than do their phenyl analogs. The butadiene copolymers which have been prepared are all richer in the thiophene-containing monomer than the charging stock with which the polymerizations were carried out, which indicates a strong tendency toward alternation in this series. The properties of a variety of new copolymers have been recorded.

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