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Structural Correlations in the Pyrolytic Degradation of Copolymers of Methyl Methacrylate and Pure *m*- and *p*-Divinylbenzene

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Summary

The rates of formation of pyrolysis products, identified by gas-liquid chromatography, of copolymers of methyl methacrylate with pure *m*- and with pure *p*-divinylbenzene show that the products derived from the meta-disubstituted unit in the meta cross-linked copolymer appear more rapidly than do those from the para-disubstituted units. This confirms the similar observation with corresponding styrene copolymers. The data from the methacrylate copolymers provide a less complicated degradative pattern, since depolymerization is the principal degradative process. The analytical data are less complicated also. The basic assumption that the relative rates of appearance of the disubstituted fragments are related to the distribution of the divinyl derived units in the network is, therefore, strengthened.

INTRODUCTION

In a previous report (*1*) we presented data establishing that the relative rates of formation of the pyrolysis products of copolymers of styrene with pure *m*- and pure *p*-divinylbenzene show that the products derived from the meta-disubstituted structural units in the meta cross-linked copolymer appear more rapidly than do those from the para-disubstituted units in the para copolymer network. This has been postulated as related to the cross-linked structures formed from the two divinylbenzene isomers. The meta isomer gives more uniformly distributed cross-links, products from which

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thus appear more rapidly in the pyrolytic degradation than does the para isomer. This has been related to differences in the copolymerization kinetics of the two copolymerizations.

Interpretation of the styrene copolymer data is complicated by the fact that styrene polymers are known to degrade by both chain-fission and progressive end-unit (unzipping) loss (2). There is a slight preference for the latter. Unfortunately, this may partially obscure the conclusion we have suggested about the distribution of the cross-linkages in the two network structures. These complications can be avoided by conducting similar degradation studies of methyl methacrylate copolymers since the methacrylates usually degrade exclusively by the unzipping process. The methacrylate–divinylbenzene copolymers would also be expected to show distributions of monomer units not unlike those shown by the styrene copolymers, since the two monomers are much alike in their copolymerization characteristics. A study of the degradation of the copolymers of methyl methacrylate with the pure *m*- and pure *p*-divinylbenzene was therefore undertaken and we wish to record the results herewith.

EXPERIMENTAL

The procedures used in the separation and purification of the *m*- and *p*-divinylbenzenes, the preparation of the bead copolymers, and the pyrolyses have been described previously (*1*). The methyl methacrylate was distilled from potassium hydroxide just prior to use; N_D^{20} 1.4134. The monomers were used immediately after distillation to remove the inhibitor and were retested at this time by refractive index, methanol precipitation, and gas-liquid chromatography to confirm purity. Beads of 30-mesh size were selected and dried at 60° at 1 mm for 48 hr before pyrolysis. Pyrolyses were made at 10-sec intervals up to 1 min and at temperatures of 545 to 560° and 620 to 635°C. This range covers that observed in many individual runs, not in each run. The average values are 552 ± 10° and 627 ± 10° from the standard deviations, δ, of approximately 5 with a precision of 1.12°C.

Gas-chromatographic analyses of typical runs are shown in Figs. 1 and 2. Retention times and percentages of products are given in Table 1. Assignments were made by comparisons of retention times with retention times of known compounds. Polymer origin of some

TABLE 1

Major Degradation Products (molar %) from Pyrolysis of Methyl Methacrylate Homopolymer and Copolymers with Divinylbenzene[a]

Products	R.T.[b]	M[c]	M/*m*-DVB[d]	M/*p*-DVB[e]
Unidentified gases	40"	—	Not calculated	—
Benzene	2'00"	0.06	0.20	0.30
Methyl methacrylate	2'50"	99.85	93.90	93.30
Unidentified (MMA)	4'15"	0.03	0.04	0.04
m-Xylene	4'35"	—	0.04	—
p-Xylene	4'50"	—	—	0.04
Styrene	6'05"	—	0.05	0.10
m-Ethyltoluene	6'50"	—	0.02	—
p-Ethyltoluene	7'10"	—	—	0.01
m-Vinyltoluene	10'00"	—	0.25	—
p-Vinyltoluene	10'25"	—	—	0.27
m-Diethylbenzene	10'50"	—	—[f]	—
p-Diethylbenzene	11'20"	—	—	—[f]
m-Ethylvinylbenzene	15'00"	—	0.07	—
p-Ethylvinylbenzene	16'15"	—	—	0.10
Unidentified (MMA)	18'30"	0.07	0.11	0.25
m-Divinylbenzene	20'20"	—	5.04	—
p-Divinylbenzene	22'45"	—	—	5.57
Unidentified (*m*-DVB)	30'25"	—	0.12	—
Unidentified (*p*-DVB)	36'10"	—	—	0.16

[a] The per cent values given are from 0.1% initiated homopolymers and an average of 0.1% and 0.5% initiated copolymers for a 60 to 70% degree of depolymerization.

[b] Retention times.

[c] Pure poly(methyl methacrylate).

[d] Methyl methacrylate/8 mole% *m*-divinylbenzene copolymer.

[e] Methyl methacrylate/8 mole% *p*-divinylbenzene copolymer.

[f] Peak obscured.

peaks were assigned by comparison with degradation products from the homopolymers. Yields were calculated from peak areas using the peak width at half-height product approximation. Data for the pyrolyses of copolymers prepared with 0.5% initiator (benzoyl peroxide) and 8% of divinyl monomer are summarized in Figs. 3 and 4 and Tables 2 and 3. Data for the copolymers prepared with 0.1% initiator do not show the marked differences observed with the 0.5% copolymers, but there is some evidence that the meta products appear more rapidly than the para products.

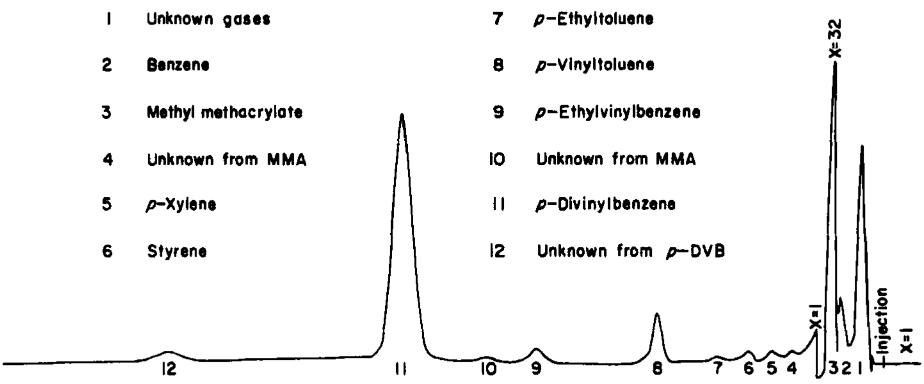

FIG. 1. Vapor-phase chromatogram of pyrolyzate from *p*-DVB/MMA (0.1% initiated) at 627°C to 90% conversion.

RESULTS AND DISCUSSION

The pyrolysis data for the methyl methacrylate copolymers with pure *m*- and pure *p*-divinylbenzenes confirm the observations with the corresponding styrene copolymers. The pyrolytic products are characteristic for the two copolymers and they are formed at different rates. The meta products appear more rapidly in the pyrolysis of the meta cross-linked material than do the para products from

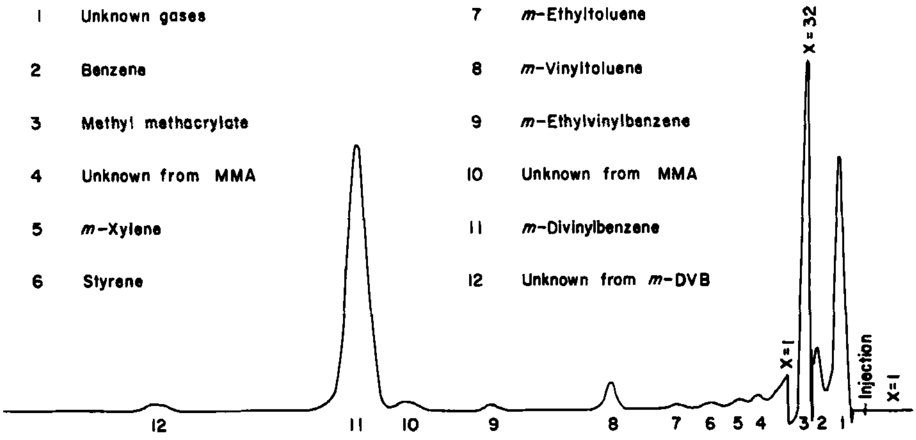

FIG. 2. Vapor-phase chromatogram of pyrolyzate from *m*-DVB/MMA (0.1% initiated) at 627°C to 93% conversion.

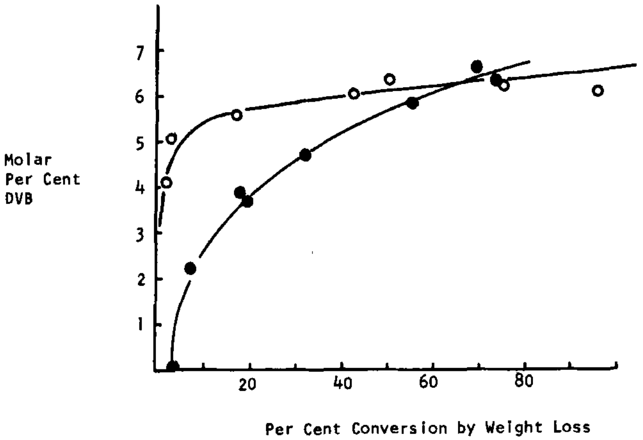

FIG. 3. Rate of appearance of divinylbenzene monomer in the pyrolysis of 8 % divinylbenzene-methyl methacrylate copolymers at 552°C. Copolymers prepared as beads with 0.5% benzoyl peroxide initiator. Open circles, *m*-divinylbenzene copolymers; closed circles, *p*-divinylbenzene copolymers.

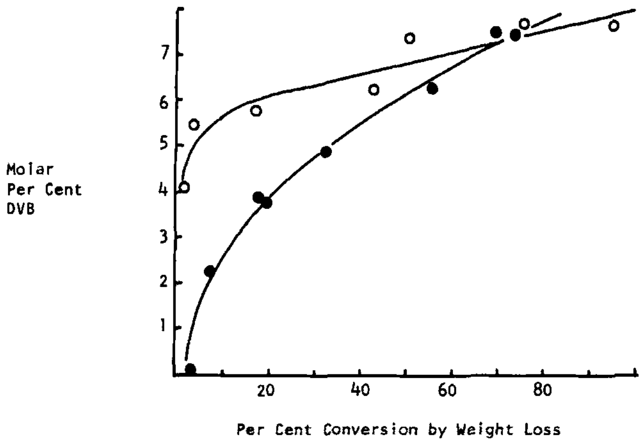

FIG. 4. Rate of appearance of divinylbenzene derived products in the pyrolysis of 8% divinylbenzene-methyl methacrylate copolymers at 552°C. Copolymers prepared as beads with 0.5% benzoyl peroxide initiator. Open circles, *m*-divinylbenzene copolymers; closed circles, *p*-divinylbenzene copolymers.

TABLE 2

Degradation Behavior of 8% *p*-DVB/MMA (0.5% b.p. init.) at 552°C

Time, sec	10	15	20	25	30	35	40	45
% Conversion	3.3	7.4	18.2	19.7	32.3	55.8	69.7	73.9
Rate, %/sec	0.33	0.49	0.91	0.79	1.08	1.59	1.74	1.64
Degradation products (molar %)								
Benzene	—[a]	0.10	—[a]	0.16	—[a]	—[a]	—[a]	—[a]
Methyl methacrylate	100.00	97.60	96.17	96.08	94.98	93.37	92.24	92.63
Unknown from MMA	—	—	Trace	0.05	0.04	0.03	0.05	0.02
p-Xylene	Trace	Trace	Trace	0.06	0.03	Trace	0.03	0.03
Styrene	—	—	—	Trace	0.06	0.03	0.05	0.04
p-Ethyltoluene	—	—	—	—	—	—	Trace	Trace
p-Vinyltoluene	—	—	—	Trace	0.11	0.21	0.39	0.47
p-Ethylvinylbenzene	—	—	—	—	Trace	0.08	0.14	0.15
Unknown from MMA	—	—	—	—	0.13	0.30	0.23	0.16
p-Divinylbenzene	Trace	2.20	3.83	3.65	4.65	5.77	6.55	6.22
Unknown from *p*-DVB	—	—	—	—	—	0.15	0.32	0.28
Total *p*-DVB products	—	2.20	3.38	3.71	4.85	6.24	7.48	6.91

[a] Peak obscured.

the para copolymer. This confirms the previous inference that, because of differences in the copolymerization kinetics, the two divinyl units are differently distributed in the chain and network. On degradation, as the chain unzips, the meta units are encountered early, are degraded earlier, and their degradation products appear earlier in the process than do the para units. The para units are presumably buried in bunches in the center of the network.

TABLE 3

Degradation Behavior of 8% *m*-DVB/MMA (0.5% b.p. init.) at 552°C

Time, sec	10	15	25	30	35	40	60
% Conversion	1.7	3.4	17.4	43.0	50.5	75.8	96.1
Rate, %/sec	0.17	0.23	0.70	1.43	1.44	1.90	1.60
Degradation products (molar %)							
Benzene	0.14	0.15	0.17	0.21	—[a]	—[a]	—[a]
Methyl methacrylate	95.77	94.39	93.86	93.43	92.47	92.21	92.22
Unknown from MMA	—	0.03	0.03	0.03	0.05	0.02	0.04
m-Xylene	Trace	0.07	0.05	0.04	0.06	0.10	0.14
Styrene	Trace	0.07	0.05	0.05	0.05	0.06	0.04
m-Ethyltoluene	—	—	—	Trace	0.03	0.09	0.14
m-Vinyltoluene	—	0.09	0.12	0.15	0.49	0.68	0.68
m-Ethylvinylbenzene	—	—	—	Trace	0.16	0.28	0.29
Unknown from MMA	—	0.14	0.14	0.13	0.13	0.10	0.11
m-Divinylbenzene	4.09	5.06	5.57	5.97	6.30	6.16	6.03
Unknown from *m*-DVB	—	—	—	Trace	0.26	0.30	0.30
Total *m*-DVB products	4.09	5.43	5.79	6.21	7.35	7.67	7.62

[a] Peak obscured.

Because the degradation of the methacrylates is relatively free of chain fission, the conclusion is established with enhanced confidence for the methacrylates as compared to the styrenes.

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REFERENCES

1. R. H. Wiley, G. DeVenuto, and F. E. Martin, *J. Makromol. Chem.*, **1**, 137 (1966).
2. N. Grassie and H. Melville, *Proc. Roy. Soc. (London)*, **A199**, 1 (1949).

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Zusammenfassung

Die Bildungsgeschwindigkeit der durch Gaschromatographie ermittelten Pyrolyseprodukte von Copolymeren aus Methylmethacrylat mit reinem meta- und reinem para-Divinylbenzol ergibt, dass die von der meta-disubstituierten Einheit im meta-verzweigten Copolymer erhaltenen Produkte schneller erscheinen als jene von den para-substituierten Einheiten. Diese Beobachtung bestätigt frühere ähnliche Ergebnisse mit entsprechenden Styrolcopolymeren. Die mit Methacrylatcopolymeren erhaltenen Daten lassen auf einen einfacheren Abbauprozess schliessen, da Depolymerisation der Hauptabbauprozess ist. Ebenfalls sind die analytischen Daten weniger kompliziert. Die grundlegende Annahme, dass die relativen Geschwindigkeiten des Auftretens der disubstituierten Fragmente mit der Verteilung der Divinyleinheiten in der Netzstruktur in Zusammenhang steht ist damit erhärtet.

Résumé

On a étudié les vitesses de formation des produits de pyrolyse, identifiés à l'aide de la chromatographie en phase gazeuse-liquide, des copolymères du méthacrylate de méthyle avec le méta- et para-divinylbenzène pur. Cette étude a montré que les produits derivés des unites metasubstituées dans le copolymère reticulé meta apparaissent plus rapidement que les

produits provenant des unités disubstituées para. Cela confirme une observation faite avec des copolymères correspondants du styrolène. Les données à partir des copolymères méthacryles fournissent un schéma de degradation moins compliqué, comme la dépolymerisation est le procedé principal de degradation. Les données analytiques sont aussi moins compliquées. L'hypothèse fundamentale, que les vitesses relatives de l'apparition des fragments disubstitués sont associées à la distribution des unités derivés divinyliques dans le réseau, est ainsi affirmée.