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Porous Polymer Carbons. V. Macroporous Carbons From Crosslinked α-Chloroacrylonitrile Polymers

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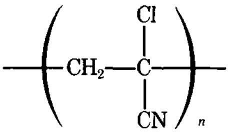
Synopsis

Suspension copolymerizations of α-chloroacrylonitrile and divinylbenzene have been carried out both with and without diluents. The polymers are macroporous except for those without diluent and of higher crosslinker content. At a fixed divinylbenzene content, the macroporosity increases with diluent content and is always higher with nonsolvating diluent. The gross morphologic features of the polymers depend on the crosslink density and on both the nature and amount of the diluent; scanning electron micrographs of typical examples are shown. Semicarbons are readily produced by dehydrochlorination. On full carbonization at 900°C, microporous carbons are produced which have some residual nitrogen-containing groups able to act as specific sites for anionic adsorbates. Homopoly α-chloroacrylonitrile fuses on heating to 900° unless it has been previously dehydrochlorinated by treatment with base. All crosslinked polymers give carbons which are pseudomorphs of the original specimens.

INTRODUCTION

Poly (α-chloroacrylonitrile)



$$\left(-\mathrm{CH_2}-\overset{\mathrm{Cl}}{\underset{\mathrm{CN}}{\mathrm{C}}}- \right)_n$$

is related to polyacrylonitrile and to poly(vinylidene chloride), both of which yield interesting carbons on pyrolysis. Thus, the initial degradation of poly(α-chloroacrylonitrile) on heating might follow one of the following routes: (a) by analogy to several other disubstituted polyolefins, a depropagation to monomer may take place; (b) by analogy to polyacrylonitrile, there may be condensation to ladder sequences; or (c) dehydrochlorination to a polyene may occur in a manner similar to that of poly(vinylidene chloride). Grassie and Grant[1] showed that the initial degradation was that of process (c) in a study largely restricted to temperatures below 200°C. Kambara and co-workers[2] investigated the pyrolysis of both poly α-chloroacrylonitrile and its chemically dehydrochlorinated derivative up to temperatures of 500°C and were able to show the formation of condensed ring sequences occurring after the development of the polyene structure.

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We have prepared network copolymers by reacting α-chloroacrylonitrile and divinylbenzene in the presence of a radical generator (benzoyl peroxide); suspension polymerizations were normally carried out at 55°C in solutions of a water-soluble polymer, usually polyacrylamide, which stabilizes the suspension against coagulation. Three series of polymer beads were prepared by this technique, one without any diluent in the monomer phase, one with a solvating diluent (nitropropane), and the third with a nonsolvating diluent (cyclohexane). Thus, precursor polymers with differing types and extents of macroporosity were synthesized similar to earlier studies with poly(vinylidene chloride).[3]

It is known[4] that polymers from α-chloroacrylonitrile are frequently discolored because of the development of some conjugated sequences under polymerization conditions, presumably due to dehydrochlorination. To minimize this effect, suspension polymerizations were made at pH 3 to give creamy-white to light-yellow copolymers. However, a fully satisfactory homopolymer could not be prepared by suspension polymerization, and an emulsion polymerization technique had to be employed. The reasons for the ready dehydrochlorination during polymerization are not clear; Grassie and Grant[4] report that polymer in solution is not discolored at ca.55° in the presence of radical generator. We have observed that polymer in the presence of monomer at 55° darkened even in the absence of radical initiator.

EXPERIMENTAL

Methods and procedures were generally as reported previously.[3] Inhibitor was removed from divinylbenzene (Koch-Light) by shaking with sodium hydroxide solutions followed by washing with water. α-Chloroacrylonitrile was twice vacuum distilled under nitrogen and was stored under nitrogen at ca.5°. Appropriate precautions were taken when dispensing this monomer, which is lachrymatory and is a vesicant. Benzoyl peroxide was recrystallized at room temperature.

Suspension polymerizations were made in continuously stirred reactors under a blanket of nitrogen at 55°; the water:monomer volume ratio was 10:1, and a polymerization time of 8 hr was normally used. The products were washed successively with water and acetone and finally vacuum dried at 40°.

Gas adsorption measurements were made in a volumetric apparatus generally similar to that described in British Standard 4359. The adsorption of dyes from aqueous solution was followed by spectrophotometric analysis of supernatants.

RESULTS

Polymers

The following nomenclature is used. Series S is that prepared with solvating diluent; NS, with nonsolvating diluent and MO, without diluent. The first number in the polymer code represents the volume fraction of divinylbenzene in the mixed monomers; for convenience, it was assumed that the technical divinylbenzene was 50% pure whereas the analytical figure is 50–

TABLE I
Properties of α-Chloroacrylonitrile Polymers

Polymer code	% Chlorine	BET surface area, $m^2 \cdot g^{-1}$ N$_2$	BET surface area, $m^2 \cdot g^{-1}$ CO$_2$	ρ_{Hg}, $g \cdot cm^{-3}$	ρ_{He}, $g \cdot cm^{-3}$	Pore volume, $cm^3 \cdot g^{-1}$
S/.200/.173				1.23		0.04[e]
S/.200/.294				1.15		0.10[e]
S/.200/.385				1.08		0.16[e]
S/.200/.455		117	163	0.90	1.32	0.36
S/.200/.556						
S/.200/.623			187	0.73	1.21	0.54
NS/.200/.173			136	0.85		0.41[e]
NS(50)/.200/.294[a]		138				
NS/.200/.294	21.9	73	164	0.75	1.20	0.50
NS(70)/.200/.294[b]		40				
NS/.200/.385			157	0.56		1.02[e]
NS/.200/.455			111	0.48	1.32	1.33
MO/.000[c]	27.4					
MO/.050		94	150	0.73	1.34	0.63
MO/.100	27.9	88	144	1.00		0.23[e]
MO/.120	23.3					
MO/.150	21.5					
MO/.200	21.8		1.3	1.18	1.20	0.01
MO/.300						
Homopolymer[d]	35.8					

[a] Polymerization temperature, 50°.

[b] Polymerization temperature, 70°.

[c] Homopolymer prepared with poly(vinyl alcohol) suspension stabilizer.

[d] Emulsion-polymerized homopolymer.

[e] Estimate assuming density in helium as 1.3 $g \cdot cm^{-3}$.

55% divinylbenzene, with most of the residual material being ethylstyrene. The second figure represents the volume fraction of added diluent. Thus, polymer S/.200/.294 refers to a mixture of 80 parts α-chloroacrylonitrile, 40 parts technical divinylbenzene, and 50 parts nitropropane. It should be appreciated that, in reality, a ternary copolymerization of α-chloroacrylonitrile (80 parts), divinylbenzene (20–22 parts), and ethylstyrene (16–18 parts) is being made with some 50–54 parts of unreactive diluent. Representative polymer properties are tabulated in Table I. Although the appropriate monomer reactivity ratios for this copolymerization system are not known, chlorine analysis of polymer recovered from one reaction (NS/.200/.294) suggests that the divinylbenzene/ethylstyrene components are the more reactive (Table II). In all cases, the chlorine analyses are typically low and are indicative of partial dehydrochlorination during polymerization; for instance, for NS/.200/.294, the theoretical value is 27.1%, while for homopolymer, it is 41.3%.

The visual appearance of fully polymerized beads varies from series to series, with some intraseries variation. Considering first the series prepared with a solvating diluent (series S). The suspension-polymerized beads appeared smooth to the eye, fairly uniform in size, and ellipsoidal rather than

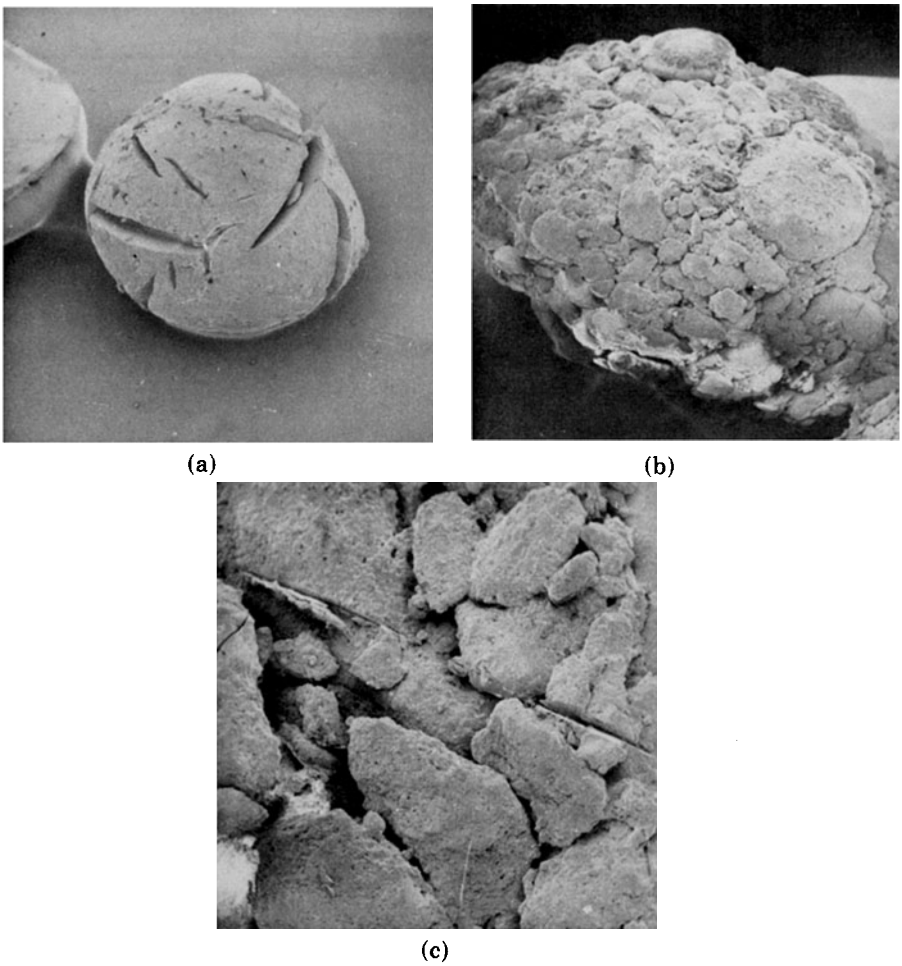


Fig. 1. Scanning electron microscopy of polymer beads: (a) S/.200/.556, normal bead (×29); (b) S/.200/.556, atypical bead (×34); (c) as (b) (×118).

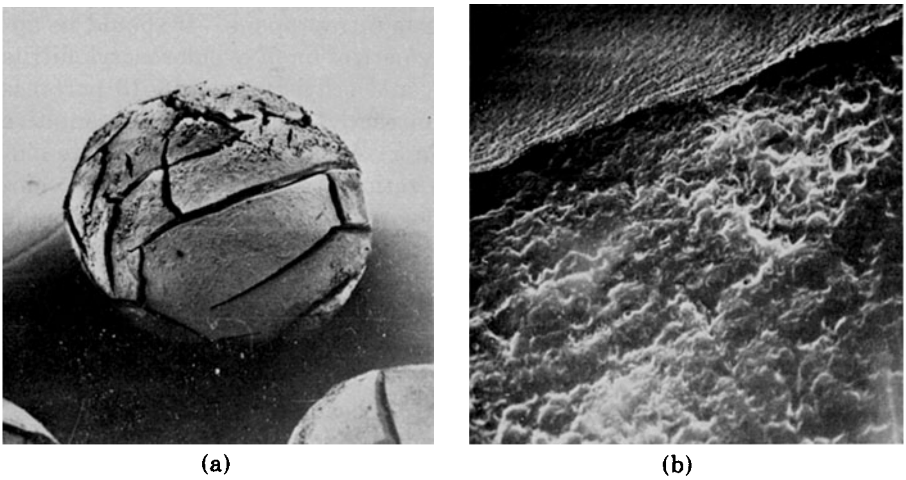
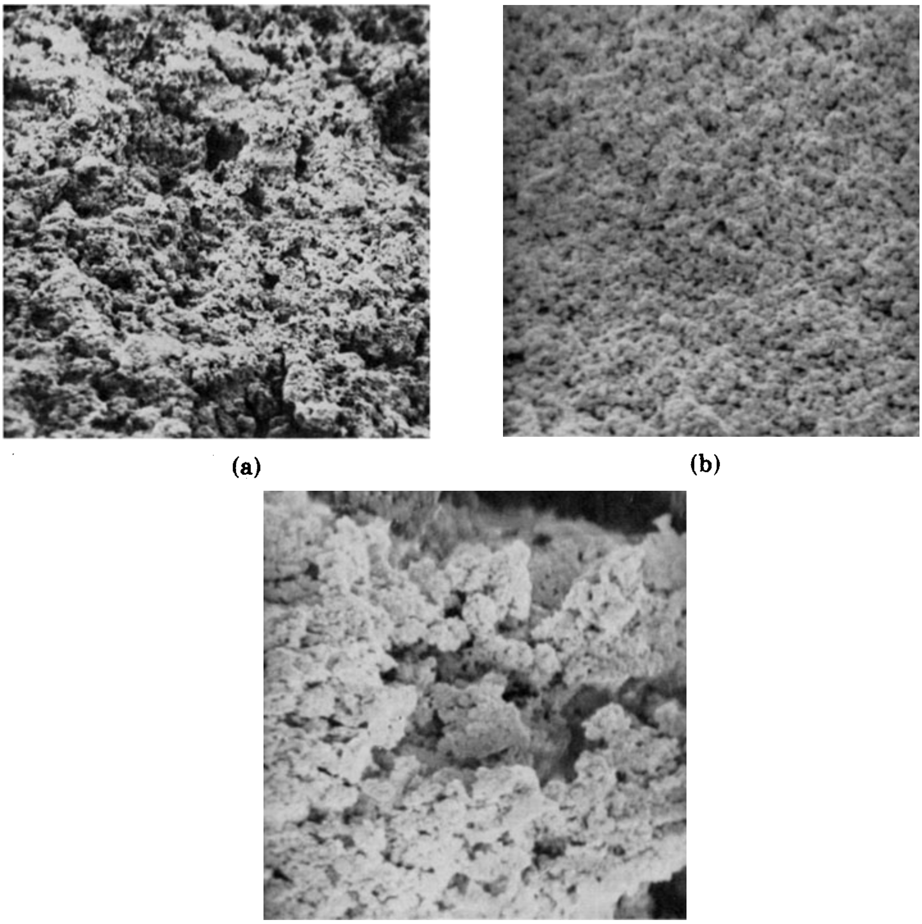


Fig. 2. Scanning electron microscopy of polymer beads: (a) S/.200/.455 (×32); (b) as (a) showing interior of surface crack (×633).



(a) (b)

(c)

Fig. 3. Scanning electron microscopy of polymer beads: (a) NS/.200/.294, porous external surface (×616) (b) as (a) fracture surface, interior of bead (×2856). (c) as (a) fracture surface, periphery of bead (×2856).

spherical. When made at a roughly constant level of agitation, the beads tended to become smaller, but more nearly spherical, as the diluent content was increased. However, at high diluent contents (e.g., S/.200/.556), a mixed product was observed, the atypical species, amounting to some 10% of the total product, taking the form of irregular agglomerates but of similar size to the "normal" beads. The atypical species is probably formed by the agglomeration of fragments of partially polymerized beads which have broken up under shear. Figure 1 shows some scanning electron micrographs of S/.200/.556. Although series S beads appeared translucent during polymerization, drying led to the development of opacity; the low-diluent polymer S/.200/.173 remained translucent but the other members of the series showed increased opacity with increasing diluent content. Surface cracks, readily apparent on scanning electron microscopic examination, are formed on drying (Fig. 2). Series S polymers were discolored to a light yellow, the more so at low diluent volume fractions.

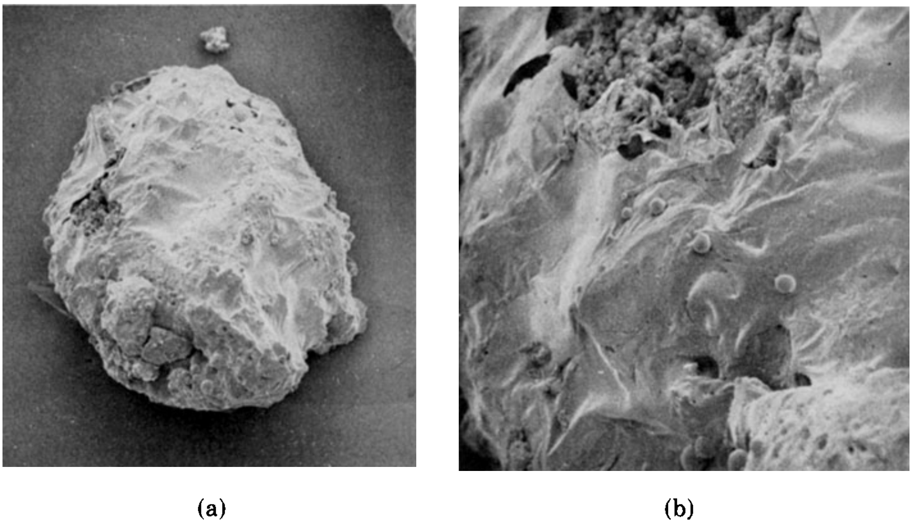


Fig. 4. Scanning electron microscopy of polymer beads: (a) NS/.200/.455 (×115); (b) as (a) (×576).

Polymer beads made with nonsolvating diluent were white and opaque and, indeed, had this appearance during polymerization. The dried beads were rough and rather irregular in shape and size. On examination in the scanning electron microscope, the beads of lower diluent content are seen to be macroporous, the more so toward the outer surface (Fig. 3); this effect is exaggerated when this formulation was polymerized at 70°. At higher diluent contents, NS/.200/.385, some small granules were also formed, and NS/.200/.455 was entirely of this granular nature and is found to be composed of a coarse agglomerate partially covered by a thin skin (Fig. 4).

The appearance of the polymers made without diluent (MO series) is related to the crosslinker content. Bead structures could not be produced below 2% crosslinker; at low crosslinker contents, the particles were irregular,

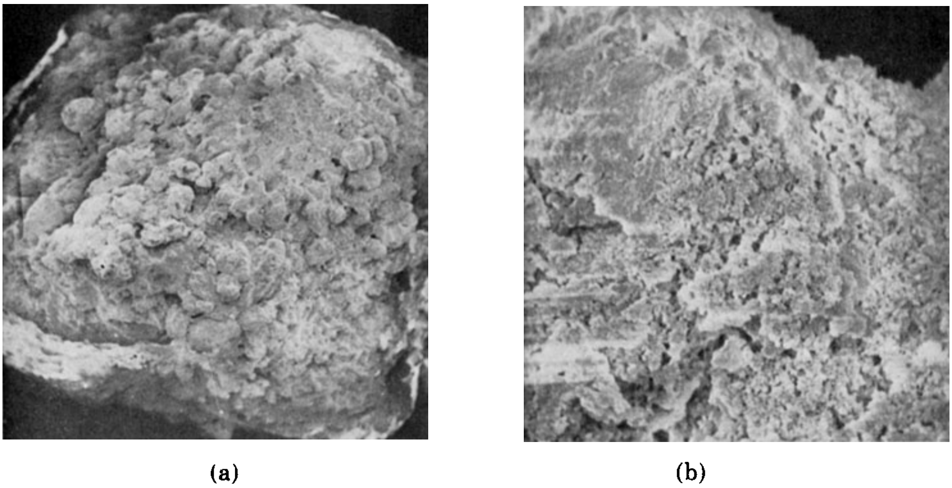
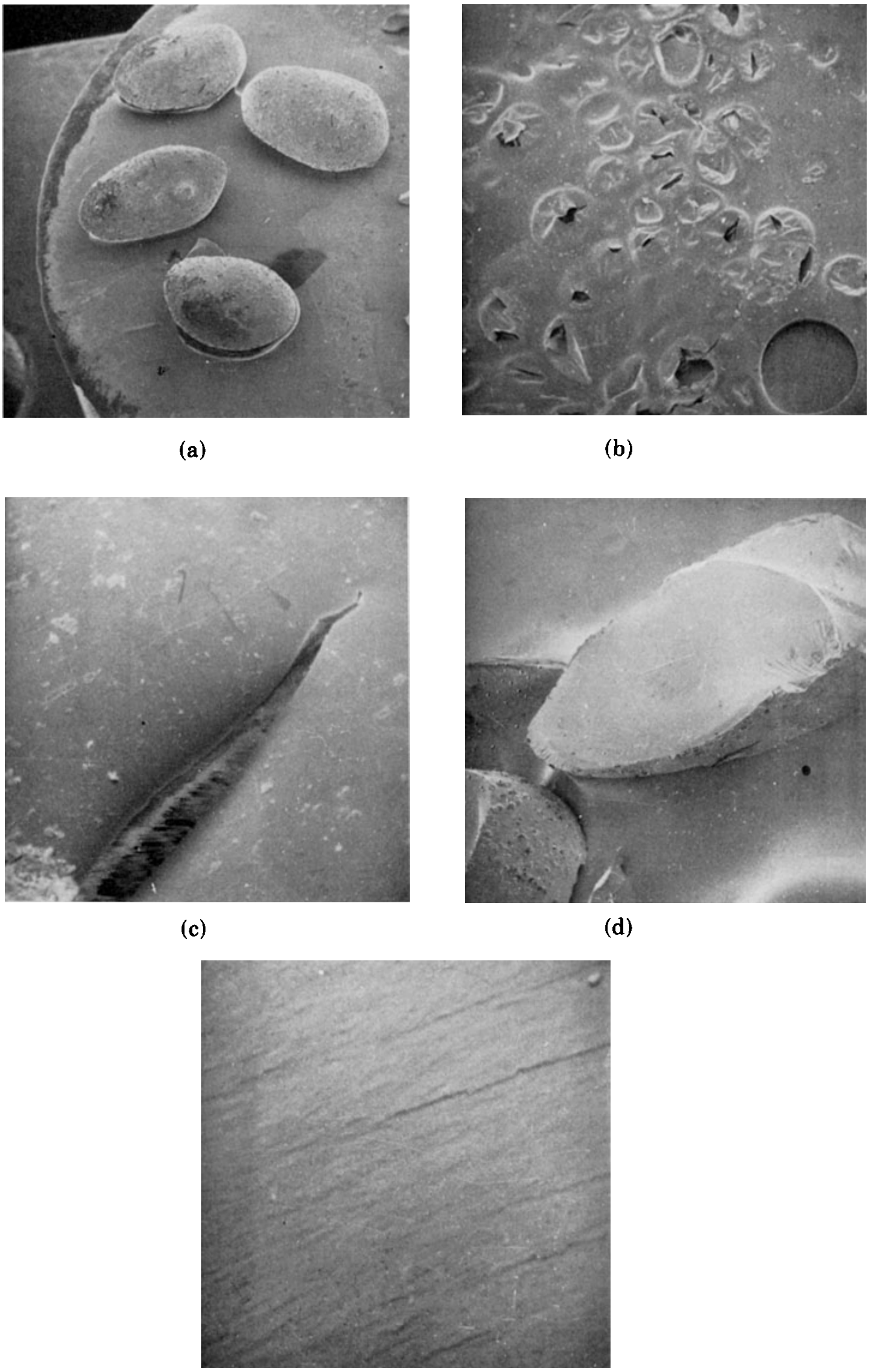


Fig. 5. Scanning electron microscopy of polymer beads: (a) MO/.050 (×30); (b) as (a), fracture surface (×2880).



(a) (b)

(c) (d)

(e)

Fig. 6. Scanning electron microscopy of polymer beads: (a) MO/.200 (×11); (b) as (a), surface (×1123); (c) as (a), surface crack (×5530); (d) as (a), cut cross section (×29); (e) as (d) (×5800).

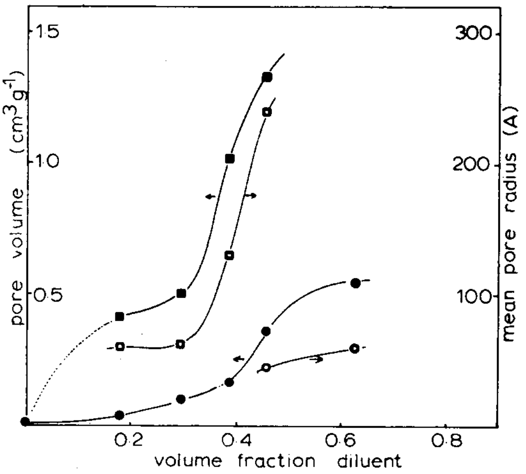


Fig. 7. Total pore volume and mean pore radius of polymers. Circles, solvating diluent; squares, nonsolvating diluent.

opaque, and off-white (Fig. 5). At 20% crosslinker and above, uniform clear, yellow beads of smooth appearance were obtained (Fig. 6a). At higher magnifications, surface "blisters" are seen (Fig. 6b) and a few cracks, but most of the surface is clearly nonporous (Fig. 6c): the interior is featureless (Figs. 6d,e). The emulsion-polymerized homopolymer was an off-white, friable powder which is seen, on electron-microscopic examination, to be composed of an aggregate of irregular subparticles.

Table I also gives some physical characteristics of the polymer particles. Surface areas were calculated by application of the BET equation to the adsorption isotherms of nitrogen (77°K) or carbon dioxide (195°K). The latter give consistently greater surface areas which might be taken as indicative of activated diffusion effects in narrow pores; the isotherm shapes are, however, not those indicative of predominantly microporous solids. Only a limited number of full adsorption-desorption isotherms were made: with both nitrogen and carbon dioxide, there was hysteresis on desorption, part of which persisted into the low-pressure region.

Total pore volumes are estimated from the difference in sample densities measured in mercury and in helium. In the solvating diluent series, the total porosity rises with diluent content as shown in Figure 7. The same trend is evident with nonsolvating diluent, but here the pore volumes are higher. Mean pore radii, assuming cylindrical pores, are calculated by combining the density data with the CO_2 surface areas; with precipitating diluents, the mean pore size depends strongly on the diluent content. In the absence of diluent and at low crosslinking contents, precipitation occurs during polymerization and some porosity is generated: at increasing divinylbenzene levels, the polymerization becomes increasingly homogeneous, and tightly crosslinked networks of low porosity are produced. It is noticeable from Table I that increasing the temperature at which polymerizations are made with the nonsolvating diluent reduces the surface area of the product.

TABLE II
Chlorine Analysis of Polymer (NS/.200/.294) Recovered During Suspension Polymerization

Time, (min)	% Chlorine
5	11.9
40	13.6
70	16.7
480	21.9

Carbons

Semicarbons were prepared by the dehydrochlorination of the copolymers. In one method the beads were placed in 10% aqueous ammonia solution at 60° for 48 hr; a more vigorous method was also employed in which the polymers were treated with potassium amide in liquid ammonia at −33° for 2 to 3 hr.[5] Semicarbons prepared by either route retained the physical appearance of the parent polymer but became brown-black in color. Elemental analyses of some semicarbons are reported in Table III; with crosslinked samples, even the more vigorous treatment does not lead to complete dehydrochlorination. Although the homopolymer was free of chlorine, some oxidation is indicated by the analytical results. Sample MO/.050/Chem has a BET surface area (CO_2,195°K) of 157 $m^2 \cdot g^{-1}$, almost identical to that of the untreated polymer.

According to Grassie and Grant,[1] during thermal degradation the dehydrochlorination reactions start at ca.150° with a peak rate of reaction at 214°. We find, on differential scanning calorimetry at 32° min^{-1}, that poly(α-chlo-

TABLE III
Semicarbon Composition

Semicarbon	% C	% H	% Cl	% N
S/.200/.623/Chem[a]	68.0	5.2	12.5	11.9
NS/.200/.294/Chem[a]	64.6	5.3	14.0	12.1
MO/.000/Chem[a]	54.5	4.7	0.0	15.1
MO/.050/Chem[b]	67.0	5.5	4.9	13.8
Homopolymer/Chem[c]	63.7	5.2	2.0	Not reported

[a] Aqueous ammonia.
[b] Potassium amide.
[c] Data of Kambara et al.[2], dehydrochlorinated with triethylamine.

TABLE IV
Properties of Polymer Carbons From Various Carbonization Conditions

Carbon	% Yield	% C	% H	% Cl	% N	BET area, $m^2 \cdot g^{-1}$ N_2	BET area, $m^2 \cdot g^{-1}$ CO_2	Solution adsorption, $\mu mole \cdot g^{-1}$ Metanil yellow	Solution adsorption, $\mu mole \cdot g^{-1}$ Methylene blue
MO/.050/300°	54	83.3	3.9	0.0	9.5	—	194	884	293
MO/.050/700°	48	89.9	1.0	0.0	5.6	110	339	1260	297
MO/.050/200°/700°[a]	—	—	—	—	—	—	336	—	—
MO/.050/900°	41	93.7	0.8	0.0	1.8	360	417	1360	299
MO/.050/Chem/900°[b]	—	—	—	—	—	—	207	—	—

[a] 12-Hr soak at 200°.
[b] Chemically dehydrochlorinated before carbonization.

TABLE V
Properties of Polymer Carbons: Standard Procedure

Carbon	% C	% H	% Cl	% N	BET area, $m^2 \cdot g^{-1}$ N$_2$	BET area, $m^2 \cdot g^{-1}$ CO$_2$	ρ_{Hg}, $g \cdot cm^{-3}$	ρ_{He}, $g \cdot cm^{-3}$	Pore volume, $cm^3 \cdot g^{-1}$
S/.200/.455/900°	—	—	—	—	—	—	1.18	1.93	0.33
S/.200/.625/900°	72.4	0.6	0.0	2.3	—	289	1.12	1.90	0.47
NS/.200/.294/900°	81.5	0.9	0.0	4.2	55	330	0.87	1.59	0.52
NS/.200/.455/900°	—	—	—	—	—	309	0.58	1.87	1.19
MO/.000/900°	77.5	2.3	0.0	5.4	—	—	—	—	—
MO/.000/Chem/900°	69.0	1.3	0.0	5.4	—	—	—	—	—
MO/.050/900°	93.7	0.8	0.0	1.8	360	417	0.98	1.99	0.52
MO/.200/900°	—	—	—	—	—	23	1.45	1.84	0.15

roacrylonitrile) undergoes an exothermic reaction between 227° and 262°; a sample held at 150° for 45 min showed the exotherm at 217° to 247°, whereas the chemically dehydrochlorinated material did not show any exotherms up to 400°.

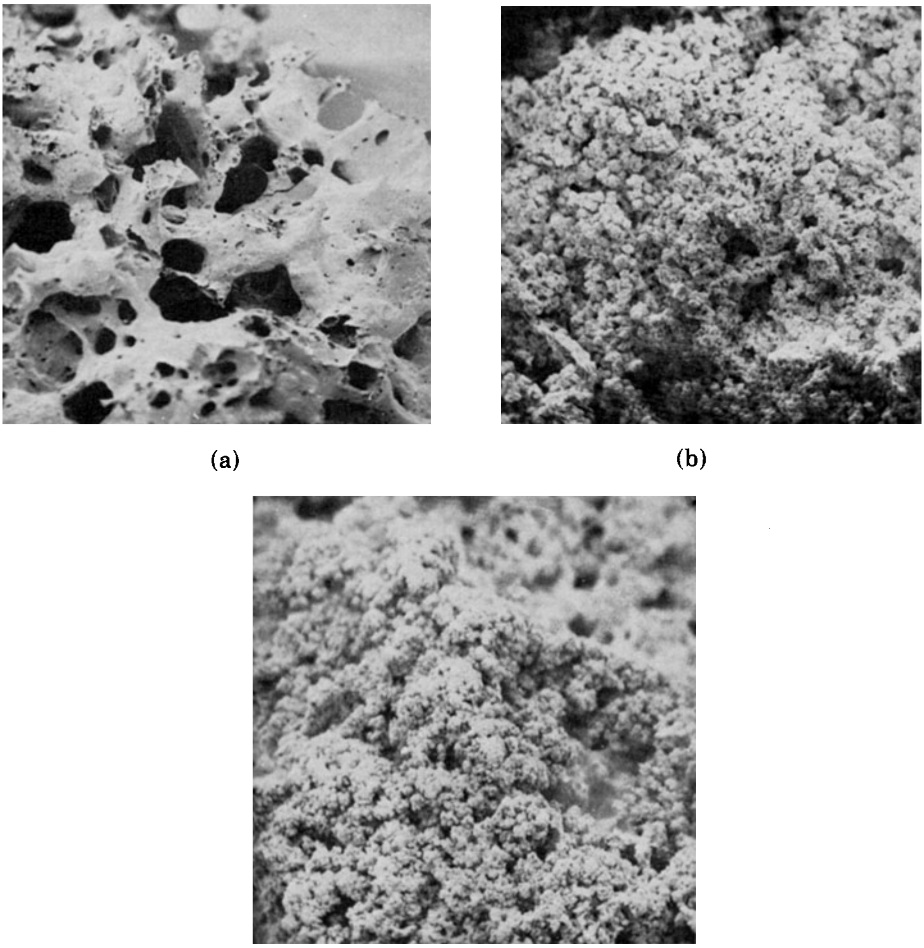

(a)
(b)
(c)

Fig 8. Scanning electron microscopy of carbons: (a) MO/.000/900 (×35); (b) MO/.000/Chem (×684); (c) MO/.000/Chem/900 (×760).

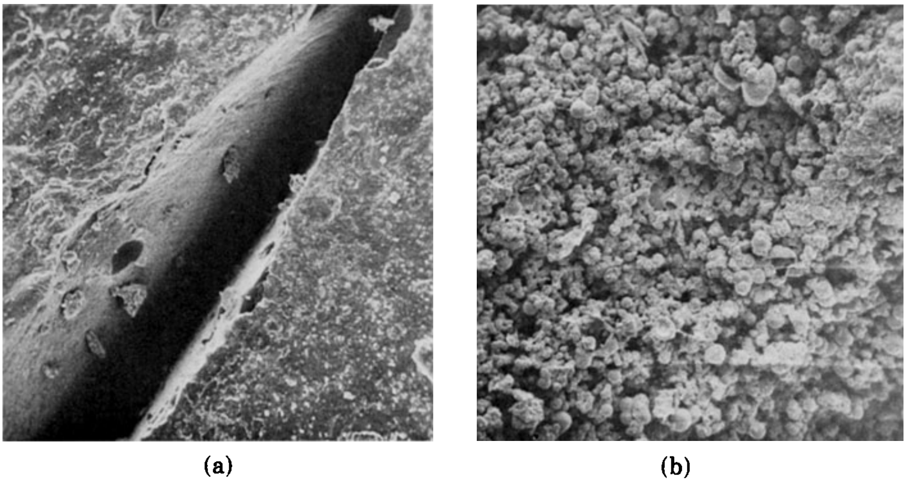


Fig. 9. Scanning electron microscopy of carbons: (a) S/.200/.556/900° (×530) surface crack; (b) S/.200/.455/900° (×510).

Samples of MO/.050 were carbonized in a vertical furnace at 1° $\min^{-1}$ under nitrogen to final temperatures of 300°, 700°, and 900° where they were held for 12 hr before cooling. These carbonizations were by the same procedure as described in the earlier report.[6] The characteristics of these carbons are given in Table IV. Following these preliminary carbonizations, a standard procedure was adopted of heating to 900°. Details of other polymer carbons, produced at 900°, are given in Table V.

Under these standard conditions, it was observed that the homopolymer fused during carbonization to a coke in 34% yield. However, if chemical dehydrochlorination is first carried out, the 900° carbon is unfused and similar in appearance to the parent polymer (Fig. 8).

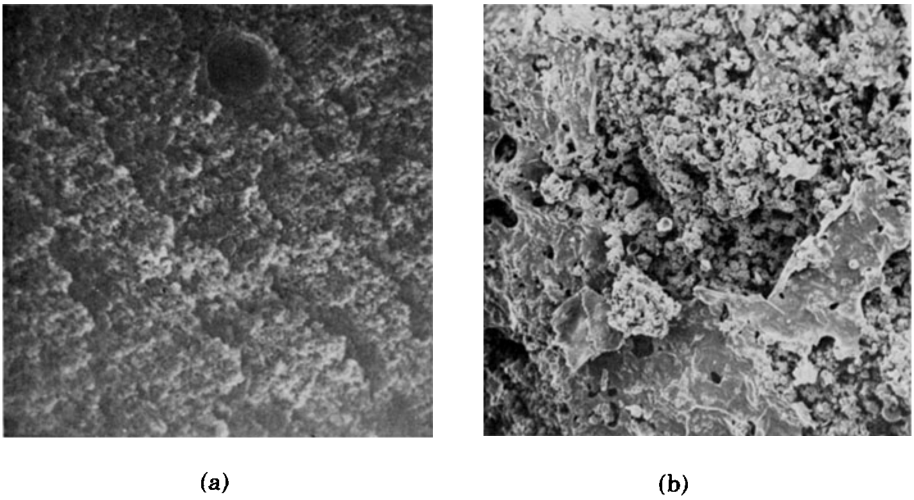
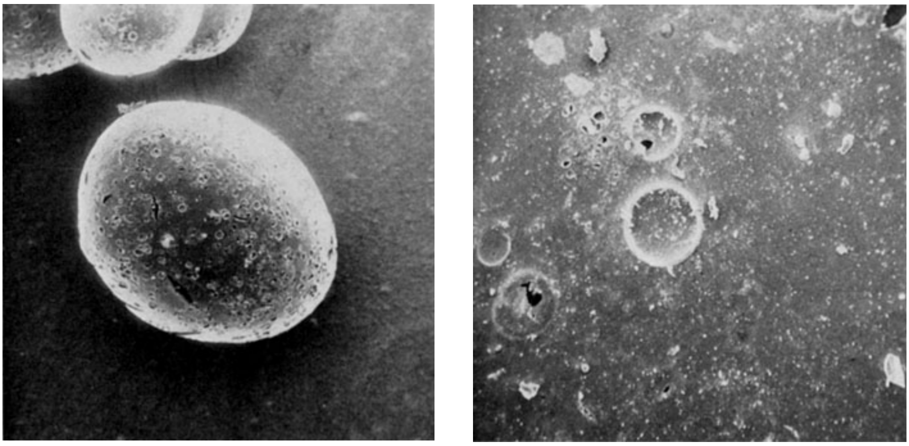


Fig. 10. Scanning electron microscopy of carbons: (a) NS/.200/.294/Chem (×2576); (b) NS/.200/.455/900° (×504) outer surface.



(a) (b)

Fig. 11. Scanning electron microscopy of carbons: (a) MO/.200/900° (×28); (b) MO/.200/900° (×276) surface.

None of the crosslinked copolymers fused on carbonization and all retained, in shrunken form, the morphologic features of the precursor polymers (Figs. 9–11). Diluent-free, highly crosslinked polymers yield hard carbons with a glossy outer surface. The net porosity tends to decrease on carbonization, while the BET surface areas increase. Thus, the mean pore radii of carbons are smaller than those of the parent polymers. These effects are attributable to the development of microporosity on carbonization, as is evident in the shape of the initial portion of the isotherm (Figs. 12 and 13).

More microporosity is developed at higher carbonization temperatures, and Table IV shows that the nitrogen and hydrogen contents are progressive-

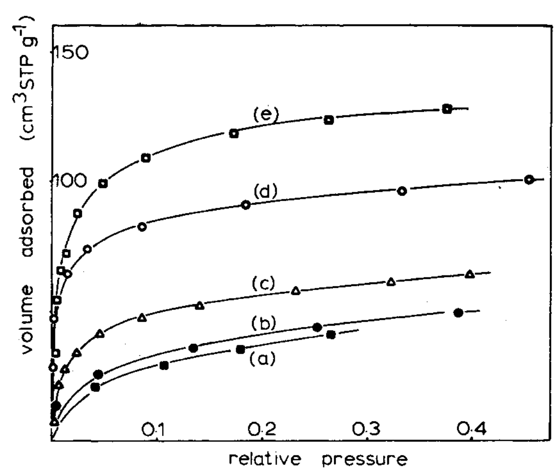


Fig. 12. Adsorption isotherms; CO_2 at 195°K: (a) MO/.050; (b) MO/.050/Chem; (c) MO/.050/300°; (d) MO/.050/700°; (e) MO/.050/900°.

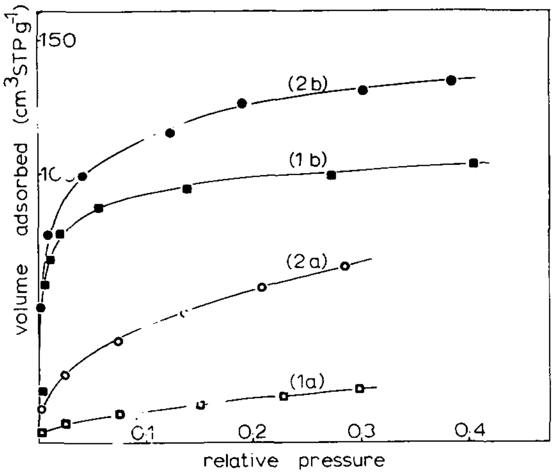


Fig. 13. Adsorption isotherms; CO_2 at 195°K: (1a) NS/.200/.294; (1b) NS/.200/.294/900°; (2a) S/.200/.625; (2b) S/.200/.625/900°.

ly reduced. The analytical figures, taken with the measured carbon yields, suggest that not all the divinylbenzene and ethylstyrene moieties are lost in carbonization. Although only a small proportion of the original nitrogen content remains in the carbon, it would seem that it exists in basic condensed structures. Certainly, the solution adsorption of the dyes metanil yellow and methylene blue, which have similar molecular areas,[7] are noticeably different in that the anionic one is adsorbed to a greater extent. On the parent polymer (MO/.050), the equilibrium adsorptions are 211 and 207 μmole·g^{-1}, respectively, while on a poly(vinylidene chloride) 900° carbon, the corresponding values are 157 and 161 μmole·g^{-1} (cf. Table IV).

CONCLUSIONS

We conclude from this work that α-chloroacrylonitrile is a useful monomer for the preparation of carbon-forming polymers. By working with various levels of crosslinking comonomer and by changing the nature and content of nonreacting diluent, it is possible to control the macroporosity of the polymer. The polymers, in turn, may be carbonized in good yield to dual-porosity carbons of high surface area and good accessibility, which retain the precursor morphology. Like the analogous case of poly(vinylidene chloride),[3,8] the homopolymer will fuse on carbonization unless the polymer morphology is locked into place in the early stage of degradation. Residual nitrogen-containing structures provide sites on the carbon for the adsorption of anionic adsorbates.

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