

POLY- α -METHYLENEGLUTARONITRILE. CHARACTERISTIC FEATURES OF SOME ANIONIC POLYMERS

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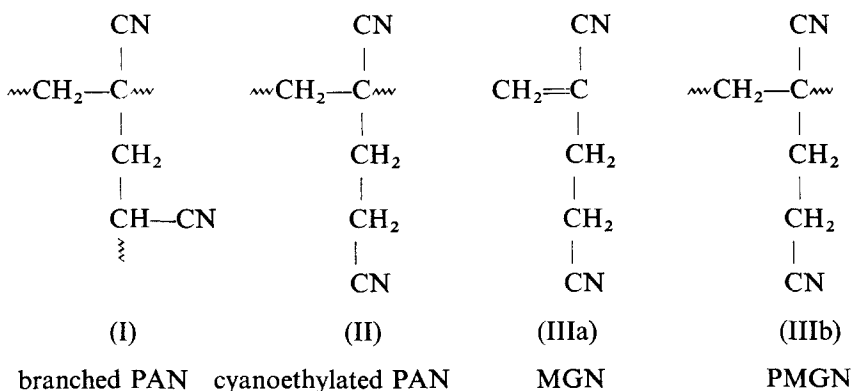
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Abstract—For (initiator)/(monomer) ratios exceeding 10^{-3} , the anionic polymerization of α -methyleneglutaronitrile in homogeneous solution in DMF (initiated by lithium-naphthalene at -35° or by diphenylmethyl-lithium at -70°) leads to fairly white polymers with yields higher than 75 per cent. Infra-red and u.v. spectrometric studies and flash pyrolysis experiments show that the nitrile functions are involved in the polymerization only to a very small extent. On the other hand, molecular weight and sedimentation measurements and hydrodynamic behaviour of the polymer in DMF solution suggest a broad polydispersity for the samples, and a very high branching density for their higher molecular weight fractions. These characteristic features are to be correlated with those of anionic polyacrylonitrile; they may be tentatively attributed to transfer to polymer at the acidic methylene group α to the nitrile function.

INTRODUCTION

WHILE studying the flash pyrolysis of polyacrylonitrile (PAN) in nitrogen,⁽¹⁾ we have noticed that the highly branched anionic PAN samples^(2–4) behave differently from their linear radical homologues. Unfortunately, the microstructure of the anionic chains is quite complex, and a simple model for branched PAN would be of great interest. As branching mainly occurs by chain transfer to polymer at the tertiary hydrogen atom^(2–4) and seems to be limited to cyanoethylation in specific cases,⁽⁵⁾ the branched structure may be represented as (I) or (II): thus, polymerization of 1-methyleneglutaronitrile [(IIIa), MGN] may lead to the required model, similar to a completely cyanoethylated PAN [(IIIb), PMGN]:



MGN is a relatively new monomer,^(6,7) and little attention has been devoted to its study. It is unable to undergo radical homopolymerization, and its monomer reactivity

ratio is low.⁽⁸⁾ On the other hand, a patent⁽⁹⁾ describes its anionic polymerization in toluene, dimethylformamide (DMF) or liquid ammonia, initiated respectively by *n*-butyl-lithium, sodium cyanide or metallic sodium; very often, the reaction gives low yields of coloured polymers of low intrinsic viscosities and they have not been further characterized.

We report here preliminary results on the anionic polymerization of MGN in a dipolar aprotic medium (DMF) and on some characteristic features of the structure and dilute solution properties of the polymer.

EXPERIMENTAL

I. Solvents, reagents and polymerization

DMF was purified according to Zaugg and Schaefer⁽¹⁰⁾ and finally dried and stored over molecular sieves (4 Å). THF was distilled over the sodium-benzophenone complex. MGN was vacuum distilled and dried over molecular sieves (4 Å); it showed a single peak in gas chromatography; it was finally vacuum distilled directly into a Schlenk vessel just before polymerization.

All the experiments involving organo-lithium reagents were carried out under a slight pressure of purified argon (50 mm Hg) in an all-Pyrex glass reactor allowing the use of vacuum and argon sweeping cycles.

Lithium-naphthalene and diphenylmethyl-lithium $[(C_6H_5)_2CH^-Li^+]$ solutions in THF were prepared according to Normant;⁽¹¹⁾ they contained about 0.5 at. Li/l. and were titrated against known amounts of acetanilide up to the coloured end-point.

For polymerization experiments, after neutralization of the solvent impurities at the selected low temperature by a few drops of initiator according to Wenger's procedure,⁽¹²⁾ the initiator was introduced and a known amount of precooled monomer (in equilibrium with crystallized monomer at -9.6°) was added dropwise with vigorous stirring into the initiator solution; at the end of the polymerization (≈ 2 hr) the reaction medium, which was almost gelified, was acidified at low temperature by 1 N HCl, and the polymer was precipitated into a large excess of methanol. Samples were purified by precipitation into methanol in a Waring Blender from a DMF solution; they were finally dried at 60° under vacuum. For comparison, some AN polymerizations were carried out similarly.⁽³⁾

II. Flash pyrolysis

Flash pyrolysis experiments were carried out in nitrogen using a Fisher-Simon apparatus characterized by a very fast induction heating of the filament up to its Curie point (in about 30 msec). Ten μ g of the sample were deposited on the filament as a film from a DMF solution. After pyrolysis (3 sec) at the selected temperature, the thermal degradation products were separated and analysed by gas chromatography (Perkin-Elmer model 900) using both flame ionization and thermal conductivity detection; chromatographic separation was carried out at 230° on Porapak Q (column of 2 m length and 1/8 in. dia; nitrogen flow rate of 25 ml/min).

III. Molecular weight and polydispersity determination

Viscosity measurements were made in an automatic capillary flow viscosimeter;⁽¹³⁾ intrinsic viscosities and Huggins constants (DMF, 25°) were calculated according to Sakai.⁽¹⁴⁾

Number average molecular weights were measured by osmometry on DMF solutions at 35° or 45° (high speed membrane osmometer Mechrolab 52) using S.S.08 cellulose acetate membranes (Schleicher & Schuell) or ultracella allerfeinst membranes (Membrane Filter Gesellschaft).

We have measured (Brice Phoenix BP 1000 V differential refractometer) the values of the refractive index increment of PMGN in a number of dipolar solvents at room temperature for $\lambda = 5460$ Å (Table 1). They depend linearly on the solvent refractive index, in good agreement with the empirical Gladstone-Dale relationship. While giving the highest dn/dc values, acetonitrile and nitromethane cannot systematically be used, since the higher molecular weight samples are not soluble in these solvents.

The values of dn/dc in DMF solution between 20° and 80° (the measurement cell at high temperatures has already been described⁽¹⁵⁾) are a linear decreasing function of temperature, characterized by a value

$$\frac{d}{dT} \left(\frac{dn}{dc} \right) = -4.8 \times 10^{-4} \text{ ml/g per degree.}$$

TABLE I. SPECIFIC REFRACTIVE INDEX INCREMENTS OF PMGN IN SOME DIPOLAR SOLVENTS

Solvent	Refractive index		dn/dc ml/g at 23° for $\lambda = 5,460 \text{ \AA}$
	n_D^{25*}	$n_{5,460\text{\AA}}^{25 \dagger}$	
Acetonitrile	1.3416	1.3429	0.179
Nitromethane	1.3796	1.3818	0.143
Propylene-carbonate	1.4209		0.109
Dimethylformamide	1.4282		0.105
γ -Butyrolactone	1.4348		0.097
Hexamethylphosphotriamide	1.4570		0.075
Dimethylsulphoxide	1.4773		0.063

* T. A. Riddick and W. B. Bunger, *Organic Solvents*, Wiley (1970).

† M. B. Huglin, *Light Scattering from Polymer Solutions*, Academic Press (1972).

Light scattering measurements (Sofica apparatus) were carried out at room temperature or at 35° after preheating the solution at 50°; we have checked the lack of any aggregation by some measurements at 55° and 80°; in this range, for a given sample, the molecular weight is independent of temperature. On the other hand, we have noticed a slight fluorescence as usually observed in the case of anionic PAN; nevertheless, the depolarization ratio was always below 0.04, and our measurements have been systematically corrected by the factor $(1 - \rho)/(1 + \rho)$.⁽¹⁶⁾

Sedimentation velocity patterns have been obtained in DMF or γ -BL at 25° or 30°, using a Beckman-model E analytical ultracentrifuge. Measurements were carried out for a single concentration at rotor speed of 60,000 rev/min.

The molar specific volume of PMGN in DMF solution at 25°, measured on a digital densimeter Anton Paar KG (Austria) model DMA-02, is 0.8157 ml/g.

The PMGN samples were fractionated by precipitation with dimethylsulphoxide/toluene-ethyl-ether (1:1 v/v) at 20° as solvent/non solvent system. This was a modification of a procedure of Kobayashi *et al.*⁽¹⁷⁾ for PAN.

RESULTS AND DISCUSSION

The anionic polymerization of MGN, carried out in DMF or in DMF-THF solution and initiated either by electron transfer (lithium-naphthalene) or double bond addition (diphenylmethyl-lithium), leads to high yields (≥ 75 per cent) of fairly white (-70°) or pale yellow (-35°) polymers. Elemental analyses of the purified PMGN-5 are as follows:

Theory C% 67.90, H% 5.70, N% 26.39, O% 0.00;

Found C% 66.75, H% 5.97, N% 25.98, O% 0.79.

It may be seen that the PMGN chain contain some unexpected oxygenated function arising from a transformation of the nitrile groups.

The polymer has solubility properties similar to radical PAN. It is soluble in dipolar aprotic solvents: dimethylsulphoxide, dimethylacetamide, dimethylformamide, N-methylpyrrolidone, γ -butyrolactone, hexamethyl-phosphotriamide, ethylene and propylene carbonate and in concentrated aqueous salt solution (NaSCN-H₂O, 50 per cent); moreover, low molecular weight samples ($\bar{M}_w < 10^5$) show unusual solubilities in acetonitrile and nitromethane as do the anionic PAN homologues.⁽³⁾

1. Infra-red spectrum of anionic PMGN (KBr disc, Perkin-Elmer 225)

The infra-red spectra of PMGN and anionic PAN are compared in Fig. 1. As expected, PMGN does not show any absorption around 1350 and 1250 cm⁻¹ because

of the lack of $\begin{array}{c} | \\ -\text{C}-\text{H} \\ | \end{array}$ methine group vibration. On the other hand, some features are common to both PAN and PMGN spectra.

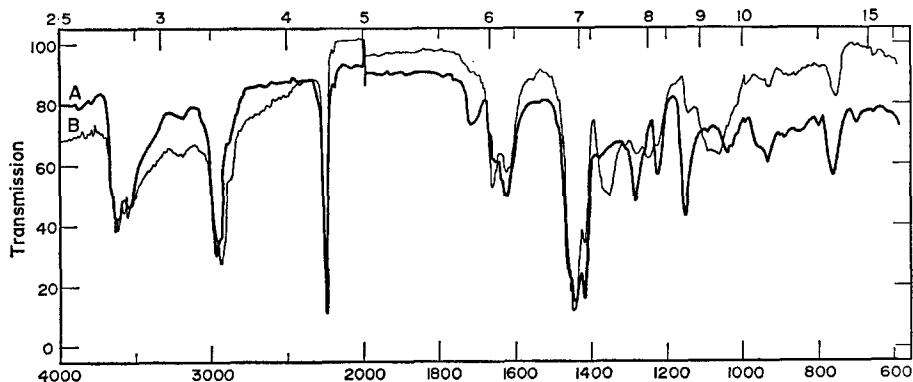
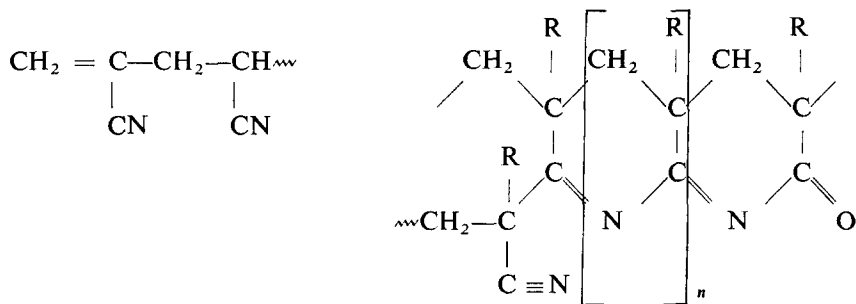


FIG. 1. Infra-red spectrum of anionic PMGN and PAN. A: PMGN-6. B: PAN prepared in the same conditions.

According to Miller,⁽⁵⁾ the absorption at 1420 cm^{-1} which may occur in PAN samples obtained by polymerization in toluene initiated by *n*-butyl-lithium is directly related to the amount of cyanoethylated units. We do observe a strong and well-defined absorption at 1420 cm^{-1} in anionic PMGN, in good agreement with Miller's assumption.

In the range $1580\text{--}1680\text{ cm}^{-1}$, PMGN shows a broad absorption with two well-defined maxima at 1660 and 1620 cm^{-1} ; both of them systematically occur in anionic PAN,⁽¹⁸⁾ but at different relative intensities. They have been correlated to terminal double bonds produced by chain transfer to monomer during the propagation [structure (IV)] but, because of their strong intensity, they may be more probably attributed to blocks of conjugated ketimine bonds $\text{--}(\text{C}=\text{N})\text{--}_n$ ^(19,20) arising from the anionic cyclization of the lateral nitrile groups [structure (V)]:

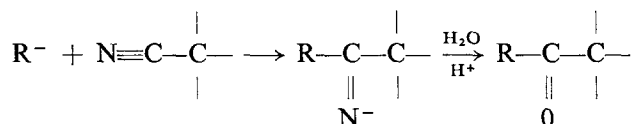


with $\text{R} = \text{H}$ (PAN) or $\text{--CH}_2\text{--CH}_2\text{--CN}$ (PMGN).

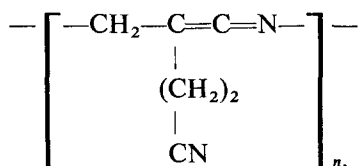
These two bands may be tentatively correlated with the weak shoulder at 2190 cm^{-1} observed in both anionic PAN and PMGN samples, which has been attributed to

β -imino-nitrile function [structure (V)] by Grassie *et al.*⁽²¹⁾ Since PMGN samples are fairly white or pale yellow, conjugated structures of type (V) are thought to be of little importance (see u.v. discussion).

The absorption at 1720 cm^{-1} ,^(22,23) common to anionic PAN and PMGN but of much greater importance for the latter, may be attributed to the carbonyl function arising from an anionic attack of a nitrile function, followed by acid hydrolysis of the ketimine bond:



The lack of any absorption in the range $2000\text{--}2045\text{ cm}^{-1}$ ⁽¹⁸⁾ rules out the possibility of ketene-imine structures arising from an unusual 1-4 propagation mechanism:



II. Ultra-violet spectrum of PMGN

Ultra-violet measurements have been carried out at room temperature on super-cooled 1 per cent solutions of PMGN in ethylene carbonate (cell thickness 1 mm, Beckman Acta 105). The u.v. spectrum is characterized by a large absorption in the range 250–350 nm with a well-defined maximum at 305 nm and a shoulder at 265 nm; their intensity is stronger when the polymerization temperature is higher (-35° vs -70°). In sharp contrast with PAN,⁽²⁴⁾ the u.v. spectrum does not change upon addition of base $[(\text{Bu})_4\text{N}^+\text{OH}^- \text{ in MeOH solution}]$, and this rules out the presence of any enolizable chromophoric group.

Following the conclusions of Beevers⁽¹⁸⁾ and Takata *et al.*,⁽²⁵⁾ these absorptions may be related to short cyclized blocks, involving probably not more than two or three adjacent units: $n = 1, 2$ in structure (V).

Longer conjugated blocks lead to an important shift in the position of the maximum absorption in the range 350–460 nm, as in PAN thermally cyclized in homogeneous DMF solution with⁽²⁵⁾ or without^(19,20) base: PMGN samples lack well-defined absorption in this range. Cyclization is highly favoured by an isotactic placement of successive monomer units in PAN.⁽²⁰⁾ It may be limited to low values in the case of PMGN, because of the greater steric hindrance around the nitrile functions. As ten or eight atom rings are unlikely, cyclization probably occurs through nitrile groups α to the backbone, in spite of the greater steric hindrance around this function.

III. Flash pyrolysis

Our results (Table 2) show that pyrolysis of PMGN is quantitative for temperatures above 400° , and that the two main degradation products are MGN and AN; the minor products cyanhydric acid, acetonitrile, methacrylonitrile and cyanopicoline have been detected only in amounts lower than 1 per cent when the temperature is below 600° .

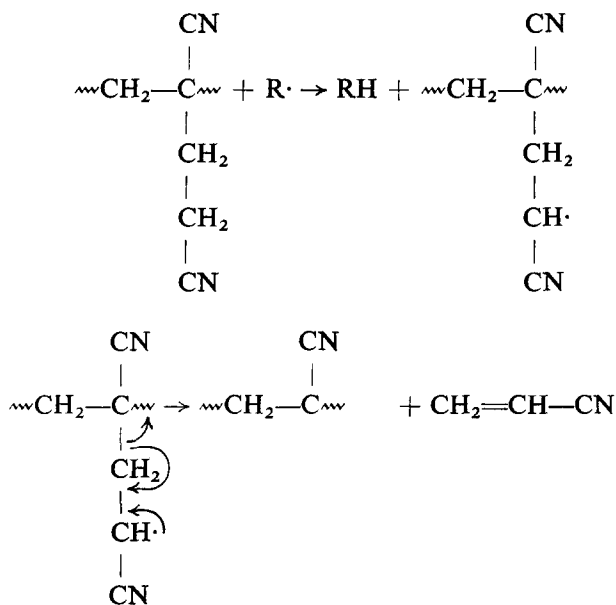
TABLE 2. FLASH PYROLYSIS OF SOME PMGN SAMPLES

		Pyrolysis temperature				
		300	400	500	600	700
PMGN-5 F ₆	Total yield %*	85	95	102	100	100
$\bar{M}_w = 280,000$	AN mole %†	12.4	11	9.2	9.3	10.7
$[\eta] = 0.950 \text{ dl g}^{-1}$	MGN mole %†	87.3	88.5	90.0	89.5	88.1
PMGN-3 F ₁	Total yield %*		93			
$\bar{M}_w = 198,000$	AN mole %†		13.7			
$[\eta] = 0.502 \text{ dl g}^{-1}$	MGN mole %†		85.7			
PMGN-1	Total yield %*		94			
$\bar{M}_w = 40,100$	AN mole %†		14			
$[\eta] = 0.310 \text{ dl g}^{-1}$	MGN mole %†		85			

* Weight percentage of total volatile products with respect to the initial sample.

† Mole percentage with respect to the total volatile products.

The relative amounts of MGN and AN seem to depend slightly on temperature and on molecular weight, but it is not possible to draw any conclusion from these preliminary results. Depolymerization of PMGN into its monomer is the expected process (note the quantitative depolymerization of poly- α -methylstyrene, polymethylmethacrylate and polymethacrylonitrile for instance). On the other hand, the presence of AN in rather large amounts in the degradation products is characteristic of the polymer structure since we have checked that, for our experimental conditions, AN cannot arise from secondary processes, like MGN degradation for instance. The most probable mechanism for AN formation involves a proton abstraction from the carbon atom α to the nitrile group followed by scission β with respect to the new radical, according to the following scheme:



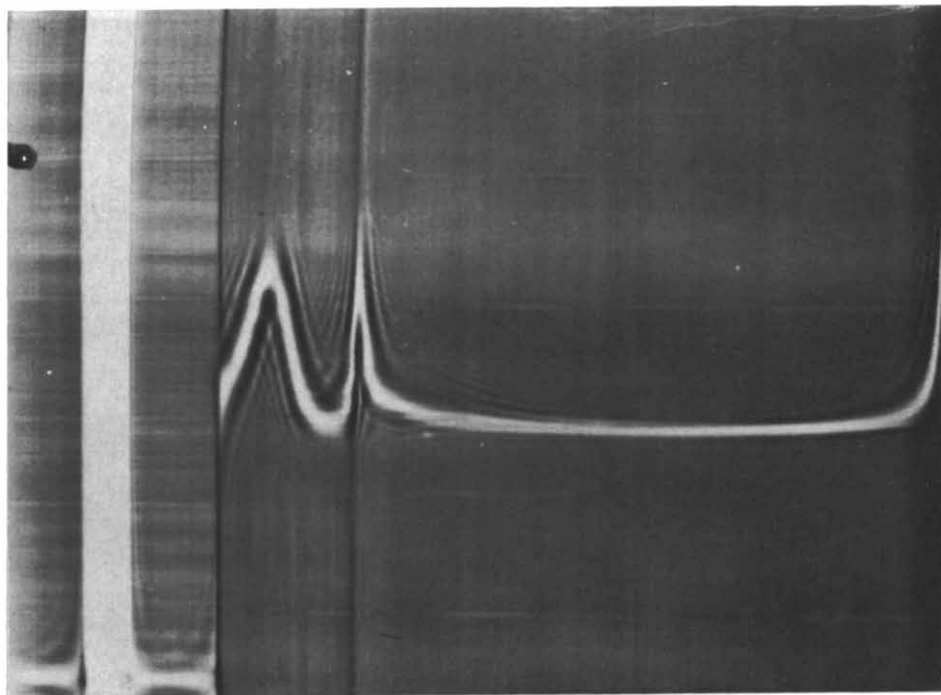
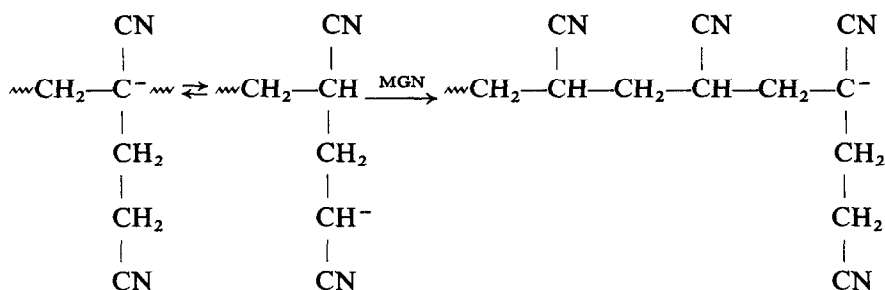


FIG. 2. Sedimentation velocity pattern of PMGN-5. (0.7 per cent in DMF solution at 25°; rotor speed of 60,000 rev/min).

(facing p. 1154)

Another reaction path arises from the possibility of a rearrangement of the terminal growing carbanion during propagation, leading to the incorporation of AN units in the polymer backbone, and then to AN monomer as the major degradation product of the PAN blocks:



However, this process seems less probable, because of the lack of any absorption of

—C—H methine group vibration in the infra-red spectrum of the polymer.

IV. Molecular weights, polydispersity and branching

1. Unfractionated samples. Our main results are given in Table 3.

Plots of the experimental results according to Kraemer's relationship ($\log \eta r/C = [\eta] - k [\eta]^2 C$) lead in most cases to negative values of the constant k , as for anionic PAN: this fact has often been interpreted as an indication of branched structures, but it has to be considered with great care, owing to the numerous factors determining the value of the different viscosity slope constants (polydispersity, thermal history of the solutions, etc. . .).

In the narrow range of low (monomer)/(initiator) ratios we have studied, experimental number average molecular weights are generally in good agreement with the theoretical values or even sometimes higher. This rules out transfer to solvent or to monomer at the acidic methylene group α to the nitrile function. On the other hand, "killing" of the carbanionic species by residual impurities and possible coupling by addition of a growing chain on a nitrile function may increase \bar{M}_n . Thus the initiator efficiency may be assumed to be nearly quantitative.

The sample polydispersities determined directly from light scattering and osmometry are quite large, in particular when diphenylmethyl-lithium is used as initiator. On the other hand, sedimentation velocity patterns clearly show a bimodal distribution (Fig. 2). From these experiments, even if made at only one concentration, it is possible to estimate the fraction of higher molecular weight: it ranges from 5 per cent (sample 2) to 26 per cent (sample 5), depending on polymerization conditions. The higher \bar{M}_w , the more important the fraction of high sedimentation velocity. Apparent sedimentation constants (at a concentration of 0.7 per cent) of the two fractions are quite distinct and may differ by a factor of 2 or more, 2.2 and 5.8, respectively, for PMGN-5.

By analogy with the well-known features of the anionic polymerization of AN, numerous factors may be taken into account to explain this high polydispersity.

TABLE 3. ANIONIC POLYMERIZATION OF MGN IN DMF AND DMF-THF SOLUTION (MGN)₀ = 0.5 mole/l.

Run	T	Initiator	Yield (%)	\bar{M}_n Theor. §	Exp.	\bar{M}_w	\bar{M}_w/\bar{M}_n	$[\eta]$ dl g ⁻¹	K _H	K _K
1*	-35	Napht.-Li	75	21,000	22,200	40,100	1.8	0.310	0.33	-0.09
2*	-40	Napht.-Li	66	24,000	24,800	56,800	2.3	0.354	0.66	
3††	-35	Φ ₂ CHLi	79	29,800	29,000	64,000	2.1	0.452	0.24	-0.28
4††	-50	Φ ₂ CHLi	76	18,000	20,000	77,500	3.9	0.357	0.26	-0.20
5†	-70	Φ ₂ CHLi	85	46,000	62,000	421,500	6.8	1.520	0.69	-0.10
6†	-70	Φ ₂ CHLi	90	40,500	68,300	257,000	3.8	1.015	0.54	-0.03
7†	-70	Φ ₂ CHLi	76	66,000	67,100	244,000	3.6	0.960	0.47	-0.06
	-70	Φ ₂ CHLi	87	61,000	79,500	294,000	3.7	1.260	0.62	-0.05

* Solvent: DMF.

† Solvent: DMF + THF (5 vol. + 2 vol.).

‡ Addition of the initiator into the precooled monomer solution.

§ \bar{M}_n theor. = $106 \times [M]/[I] \times \text{yield } \% \times k$ with $k = 2$ for napht.-Li and $k = 1$ for Φ₂CHLi.

Various initiating species may arise from double bond or nitrile addition and from proton abstraction reactions on the monomer⁽²⁷⁾ by the organo-lithium reagent; on the other hand, chain branching by transfer to polymer may occur to a large extent in a dipolar aprotic solvent like DMF.⁽²⁻⁴⁾ Both processes are known to induce a marked broadening of the molecular weight distribution, but it is more difficult to account for the bimodal shape of the sedimentation pattern; such bimodal distributions have been noticed for anionic PAN obtained in a non-polar solvent.⁽⁵⁾ Finally, PMGN-3 and, to a greater extent, PMGN-4 show the strongest polydispersities: this may be tentatively correlated with the fact that they have been obtained by addition of the initiator to the monomer solution.

In spite of the polydispersities of the samples and of their bimodal molecular weight distributions, the experimental values of $[\eta]$ and \bar{M}_w correlate reasonably well, fitting the following Mark-Houwink-Sakurada relationship:

$$[\eta] \text{ dl/g} = 3.16 \times 10^{-4} \bar{M}_w^{0.65} \text{ DMF/25}^\circ \text{ (Fig. 3).}$$

The only exception is PMGN-3, which lies far below the straight line, showing a very low intrinsic viscosity: this is attributed to a highly branched structure (see below). The radius of gyration of sample 4 is $(R_z^2)^{1/2} = 240 \text{ \AA}$ for $\bar{M}_w = 421,000$ and $[\eta] = 1.5 \text{ dl/g}$; this value shows at least qualitatively the existence of branching but, due to the high polydispersity of the sample, more precise discussion is impossible.

2. *Fractionated samples.* The experimental results obtained on the higher molecular weight fractions arising from samples 3 and 5 are given in Table 4 and plotted in Fig. 3.

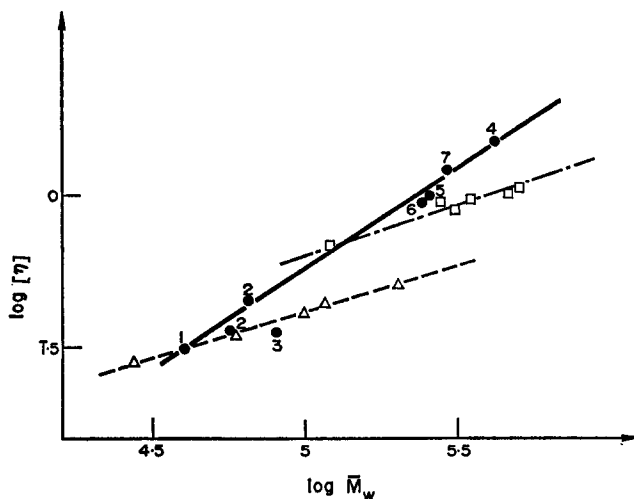


FIG. 3. Mark-Houwink-Sakurada relationships for PMGN in DMF solution at 25°. \bigcirc —Unfractionated samples (—); \triangle —PMGN-3 fractions (-----); \square —PMGN-5 fractions (---).

The efficiency of the fractionation system is poor, especially for the higher molecular weight polymer (sample 5). Nevertheless, the different experimental values correlate to:

$$[\eta] \text{ dl g}^{-1} = 1.32 \times 10^{-2} \bar{M}_w^{0.30}, \text{ for PMGN-3}$$

DMF/25°

$$[\eta] \text{ dl g}^{-1} = 1.26 \times 10^{-2} \bar{M}_w^{0.34}, \text{ for PMGN-5.}$$

TABLE 4. MOLECULAR CHARACTERISTICS OF SOME PMGN FRACTIONS

PMGN-3					PMGN-5					
Fraction	w_i (%)	$[\eta]$ (dl g ⁻¹)	\bar{M}_w	a^* (Å)	Fraction	w_i (%)	$[\eta]$ (dl g ⁻¹)	\bar{M}_w	$(R_g^2)^{1/2}$ (Å)	a^* (Å)
1	13.8	0.502	198,000	125	1	6.0	0.896	310,000	†	205
2	15.4	0.450	116,000	105	2	1.9	1.026	453,000	240	235
3	8.1	0.410	99,000	100	3	2.6	0.968	345,000	†	215
4	7.9	0.352	59,500	85	4	2.5	1.090	491,000	260	240
5	8.0	0.286	27,000	65	5	14.7	0.950	280,000	†	200
					6	2.9	0.675	121,000	†	150

* Calculated radius of the model porous sphere molecule according to Seely's relationships.⁽³⁰⁾

† Too weak to be measured.

DMF being a good solvent for these fractions (the values of their second virial coefficient lie between 0.8×10^{-4} and 1.3×10^{-3} at 35° and remain positive at 23° , this result is quite surprising, since we obtain much lower values of the exponent α of the M.H.S. relationship than for the unfractionated samples. We can try to explain this anomalous behaviour by taking into account the bimodal distribution of molecular weight shown by ultracentrifugation. Let us assume that the fast sedimentating species are highly branched and therefore that they have a very low value of the exponent α , and that the slower sedimentating species are much less branched or even linear. Since we have studied only the higher molecular weight fractions, we deal with the highly branched structures which explain the observed low value of the exponent α . On the other hand, in the whole sample, the highly branched fraction has a very low intrinsic viscosity, but contributes only to an increase of \bar{M}_w , this increase being probably constant for all the samples: thus, the same low value of the exponent α cannot be obtained for the unfractionated samples. It can also be understood in the same way that the experimental points of the whole sample can lie either below (sample 3) or above (sample 5) the line related to its higher molecular weight fractions.

Because of the lack of well-defined linear PMGN, the hydrodynamic behaviour of the samples cannot be described by the theories related to star, comb-shaped or randomly-branched polymers.^(28,29) Moreover, the observed decrease of the exponent of the M.H.S. relationship is so high that it suggests a very dense packing of the branches in a nearly spherical molecule. According to Seely,⁽³⁰⁾ the hydrodynamic properties of very highly branched polymers may be treated in a simple way, considering that the monodisperse polymer chains behave as porous spherical molecules of radius a , permeability K , porosity ϵ and density ρ_1 and assuming that K and ϵ values are independent of molecular weight; molecular weight, molecular dimensions and intrinsic viscosity are related by the following equations:

$$M = \rho_1 (4 \pi N a^3/3) (1 - \epsilon) \quad (1)$$

$$[\eta] = A/[1 + B M^{-2/3}] \quad (2)$$

with

$$A = 5/[2(1 - \epsilon)\rho_1] \text{ and}$$

$$B = 10 K[4\pi N(1 - \epsilon)\rho_1/3]^{2/3}.$$

In spite of the polydispersity and of the probably non-uniform branching density of the samples, the experimental results reasonably fit Eqn. (2) (Fig. 4); moreover, the values of the radius of gyration deduced from light scattering experiments agree with the calculated values of the sphere radius a for fractions 2 and 4 of PMGN-5; see Table 3. This may be a coincidence, but this model seems to be in accord with the experimental results.

The calculated values of porosity ϵ and permeability K are, respectively, 0.968 and $5.620 \times 10^{-14} \text{ cm}^2$ for PMGN-3 fractions, compared with 0.988 and $3.785 \times 10^{-13} \text{ cm}^2$ for PMGN-5 fractions: in spite of a lower molecular weight, PMGN-3 is characterized by a higher branching density and a less porous structure, probably because of the higher polymerization temperature (-35° rather than -70°). It has to be pointed out that the same hydrodynamic model of a porous sphere molecule may be successfully applied to the anionic PAN samples prepared in the same conditions as PMGN.⁽³¹⁾

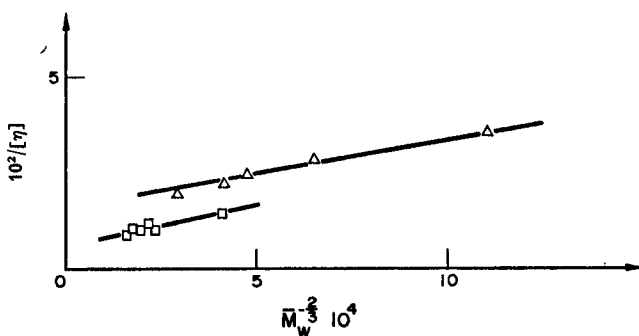
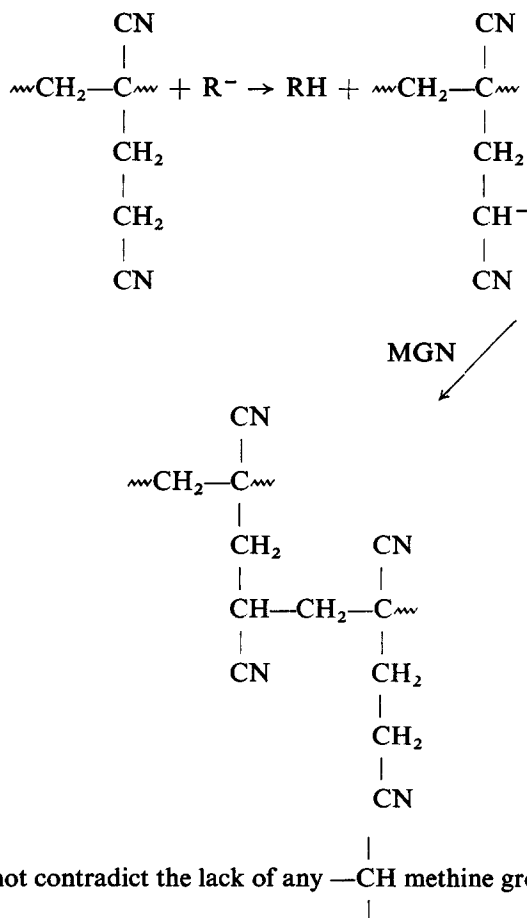


FIG. 4. Seely's correlation between $[\eta]$ and \bar{M}_w for PMGN in DMF solutions at 25°. Δ —PMGN-3 fractions; \square —PMGN-5 fractions.

In order to explain these highly branched structures, different chemical mechanisms may be assumed.

As shown by spectrometric studies, the CN groups are not involved to a great extent in the polymerizations, and branching probably arises from transfer to polymer at the acidic methylene group, according to the following scheme:



infra-red spectrum: dilute solution properties are very sensitive to branching, even if the number of branching points is too weak for infra-red analysis.

This situation is obviously very similar to that of AN polymerization characterized by transfer to polymer at the tertiary hydrogen atom.⁽²⁻⁴⁾ Nevertheless, it is not possible to exclude any addition of growing chains on the nitrile functions: this reaction, if it is limited to low extent, does not greatly affect the nitrile band in the infra-red spectrum, but it yields keto groups which have effectively been observed in greater amounts than in anionic PAN. An intramolecular process has no effect on the molecular weight but leads to macro rings of lower intrinsic viscosity; an intermolecular process is similar to a coupling reaction and it does not greatly change \bar{M}_n , but contributes to the formation of highly branched structure, and can perhaps explain the bimodal molecular weight distribution.

CONCLUSION

The anionic polymerization of MGN at low temperature in homogeneous DMF solution leads with high yields to nearly white polymers. Spectroscopic and flash pyrolysis studies show that the PMGN chain cannot be quantitatively described as a regular head-to-tail succession of monomeric units: chemical irregularities such as very short cyclized blocks and keto functions may occur in small amounts. The hydrodynamic properties in dilute DMF solution suggest a highly polydisperse and branched structure, arising probably from transfer to the acidic methylene groups in the polymer, which are α to the nitrile function.

Owing to their similar chemical structure, MGN and AN may show similar behaviour in anionic polymerization. Our results have to be considered only as representative of the particular experimental conditions. The proton abstraction reactions and the nucleophilic addition to the double bond or to the cyanogroup between initiator and growing living chains, on the one hand, and monomer or polymer, on the other hand, are competitive processes in both the initiation and the propagation steps; all the factors which affect their relative importance may lead to very sensitive differences in polydispersity and branching density. In this sense, the natures of the solvent and the counter-ion and the temperature are important; it may be expected that polymerizations in a non-polar solvent, such as toluene, should lead to much less branched polymers, as was observed for AN.^(3,5) All these aspects obviously need further studies, but this is far beyond the scope of our present work.

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Résumé—Pour des rapports (initiateur)/(monomère) supérieurs à 10^{-3} , la polymérisation anionique de l' α -méthylène-glutaronitrile en phase homogène dans le DMF, amorcée à -35° par le naphthalène-lithium ou à -70° par le diphenylméthyl-lithium, conduit avec des rendements supérieurs à 75 pour cent, à des polymères blancs. La spectrométrie i.r. et u.v. et la pyrolyse éclair en atmosphère inerte montrent que le groupement nitrile ne participe pratiquement pas à la polymérisation. Les mesures de masse moléculaire, de vitesse de sédimentation et le comportement hydrodynamique en solution diluée dans le DMF mettent en évidence la large polydispersité des polymères bruts et le très haut degré de ramification de leurs fractions de poids moléculaire élevé. Ces résultats et leur analogie avec ceux relatifs aux polyacrylonitriles obtenus dans des conditions identiques suggèrent que la polymérisation est caractérisée par une importante réaction de transfert au polymère au niveau du méthylène acide activé par la fonction nitrile.

Sommario—Con rapporti di iniziatore/monomero superiori a 10^{-3} , la polimerizzazione anionica dell' α -metilene-glutaronitrile in soluzione omogenea in DMF (iniziata con litio-naftalene a -35° oppure con difenilmetil-litio a -70°) conduce a polimeri alquanto bianchi con rendimenti maggiori del 75 percentuale. Studi spettrometrici all'infrarosso e all'ultravioletto, come pure esperimenti di pirolisi istantanea, mostrano che le funzioni nitrile entrano in gioco nella polimerizzazione solamente in piccola misura. D'altro canto, le misurazioni di peso molecolare e di sedimentazione, come pure il comportamento idrodinamico del polimero in soluzione DMF, lasciano supporre un largo grado di dispersione per i campioni ed un'elevatissima densità di diramazione per le frazioni a più elevato peso molecolare. Tali caratteristiche vanno messe in relazione con quelle del poliacrilonitrile anionico; esse potrebbero essere attribuite al trasferimento in polimero in corrispondenza del gruppo acido di metilene α nella funzione di nitrile.

Zusammenfassung—Bei Molverhältnissen Initiator/Monomeres $> 10^{-3}$ führt die bei -70°C durch Lithium-Naphthalin oder Lithium-Diphenylmethyl initiierte anionische Polymerisation des 2-Methylenglutarsäuredinitrils in homogener DMF-Lösung zu weißen Polymeren mit einer Ausbeute > 70 pro cent. IR- und UV-spektroskopische Untersuchungen sowie flash-Pyrolyse unter Inertgas zeigen, daß die Nitrilgruppe praktisch keinen Anteil an der Polymerisation nimmt.

Molekulargewichtsmessungen, Sedimentationsexperimente sowie das hydrodynamische Verhalten der Polymeren in verdünnter DMF-Lösung bestätigen eine große Molekulargewichtsverteilung der erhaltenen Polymeren ebenso wie einen sehr hohen Verzweigungsgrad bei höheren Molekulargewichtsfractionen. Die erhaltenen Resultate zeigen viel Ähnlichkeit mit dem charakteristischem Verhalten der unter gleichen Bedingungen hergestellten Polyacrylnitrile und erlauben die Annahme, daß die Polymerisation von einer bedeutenden, durch die Nitrilgruppen angeregten Übertragungsreaktion mit dem sauren Methylen des Polymeren begleitet wird.