TABLE I
Absorbance Ratios for 100% and 0% Isotactic Contents in Polypropylene

Standard for 100% isotactic content	Absorbance ratio	Standard for 0% isotactic content	Absorbance ratio
Theoretical 100% crystalline material[3] (sp. vol. = 1.069)	A 1167 cm.$^{-1}$/A 974 cm.$^{-1}$ = 1.055	Ether-soluble extract	A 1167 cm.$^{-1}$/A 974 cm.$^{-1}$ = 0.347
Residue from heptane and ether extracts	A 997 cm.$^{-1}$/A 974 cm.$^{-1}$ = 1.00	Acetone-soluble extract	A 997 cm.$^{-1}$/A 974 cm.$^{-1}$ = 0.180
Highly isotactic experimental polypropylene	A 841 cm.$^{-1}$/A 974 cm.$^{-1}$ = 0.960	Molten polypropylene (180°C.)	A 841 cm.$^{-1}$/A 974 cm.$^{-1}$ = 0.000

TABLE II
Polypropylene Isotacticities Obtained from Flory's Theory and by Infrared Methods

Sample no.	Insoluble in:	Soluble in:	M.p., °C.	Flory's theory	Infrared, cm.$^{-1}$ band		
					1167	997	841
I	Diethyl ether	n-Pentane	110–115	62	59	12	28
I	n-Pentane	n-Hexane	122–126	68	68	29	43
I	n-Hexane	n-Heptane	136–140	76	72	28	46
I	2-Ethylhexane	n-Octane	142–145	80	79	52	69
I	n-Octane		155–165	90	93	85	95
II	2-Ethylhexane	n-Octane	173–174	99	97	85	98

line species, $T_m°$, is taken as 176°C.; ΔH_I is the heat of fusion and has a value of 2600 cal./mole unit.[7] Therefore, by determining the melting point T_m of a polypropylene sample the mole fraction of isotactic segments, N_I, may be calculated. Since only one molecular species is involved, the mole fraction and the weight fraction are the same. Thus values obtained from the melting point formula can be compared directly with values obtained from infrared data.

A series of extractions was carried out on two experimental polypropylene samples. A melting point was determined for each fraction extracted. Films (ca. 1 mil) of the various fractions were molded and annealed overnight at 105°C.

Per cent isotacticities were determined from Flory's equation and from the three different infrared methods.

The results are listed in Table II. At high isotactic contents all three methods agree fairly well, but at isotactic contents of 80% and less only the method based on the 1167 cm.$^{-1}$ band is found to give good agreement with values from Flory's theory.

Therefore, it appears that the method suggested by Brader[3] gives a good measure of the isotactic content for polypropylene, at least in the 60–100% range.

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High Molecular Weight Polycationics

Since polyvinylpyridine was quaternized and studied by Fuoss and Strauss,[1] many studies of polyvinylpyridinium systems have been made, by these authors and their coworkers, and by others.[2,3] Our interest has been directed to a different class of polyquaternaries.

Vinylbenzyl chloride was chosen as a starting monomer, because it can be readily polymerized[4] and copolymerized,[5] and its product polymers may then be used to prepare polycationics of widely varying properties and stabilities. The free radical polymerization of vinylbenzyl chloride requires care, because of the reactivity of the chloromethyl group. Mass polymerization at high temperatures results in crosslinking, while emulsion polymerizations at 50°C.

and higher result in excessive hydrolysis. Jones and co-workers[5] avoided these problems by low temperature ionic polymerization with BF_3. Arcus and Salomons[4] mass-polymerized with azobis(isobutyronitrile) under mild conditions to about 50% conversion, obtaining linear poly(vinylbenzyl chloride) (PVBC) of rather low molecular weight ($[\eta] = 0.25$).

In the present work, monomer obtained by the method of McMaster and Stowe[6] (²/₃ para-isomer, ¹/₃ ortho-isomer) was polymerized in emulsion at 30°, using $K_2S_2O_8$–$Na_2S_2O_5$ (each at 0.0034 mole/mole monomer) as the initiating system. Conversions of 90–96% are obtained in 16–22 hr. Polymer molecular weights are regulated by additions of small amounts of transfer agent. The intrinsic viscosities (in toluene at 25°) of PVBC thus prepared with 0.010 and 0.100% of tert-dodecyl mercaptan are 2.10 and 0.96 cks., indicating approximate molecular weights (based on polystyrene constants[7]) of 1.4×10^6 and 4.5×10^5, respectively. Introduction into the polymerization mixture of small amounts of divinylbenzene results in the formation of cross-linked microgels,[8] wherein each latex particle is one macromolecule. A typical "latex molecule" of 600 A. diameter has a molecular weight of about 8×10^7.

Nucleophilic displacements upon PVBC in highly polar media are rapid and easy. To 25.0 g. of latex suspension containing 26.6% PVBC was added 11.15 ml. of a 25% aqueous solution of trimethylamine (100% of theory) and 56.9 g. water. The mixture was shaken and allowed to stand at room temperature, whereupon within an hour the water-thin opaque latex system was transformed to a clear firm gel of poly(trimethyl(ar-vinylbenzyl)ammonium chloride) (10% solids). The gel is dilutable with water in all proportions, yielding clear stable solutions. Replacement of the initial dilution water with a water-alcohol mixture (33.85 g. water, 23.05 g. isopropanol) results in a clear viscous syrup containing the same concentration of product polymer.

To 0.0479 gram-equivalents of PVBC in 50 ml. water was added 100 ml. methanol and 0.0958 mole (100% excess) of N,N-dimethyl-n-dodecylamine (Armour's Armeen DM12D) and the mixture shaken for 5 days at room temperature, whereupon a viscous buttery top layer was obtained, composed of polymer and excess amine. The product polymer, poly(dimethyl-n-dodecyl(ar-vinylbenzyl)ammonium chloride), is water-insoluble but is readily soluble in methanol, isopropanol, N,N-dimethylformamide, and diethylene glycol.

To 0.290 gram-equivalents of PVBC in 200 g. of wet latex was added 236.5 g. water, 198.7 g. isopropanol, and 0.435 mole (50% excess) of dimethyl sulfide, and the mixture shaken for 16 hr. at room temperature, whereupon a clear viscous syrup of poly(dimethyl(ar-vinylbenzyl)sulfonium chloride) was obtained (10% polymer solids).

The reaction products of PVBC with trimethylamine and with dimethyl sulfide are both soluble in water, methanol, and ethylene glycol, and insoluble in isopropanol, dioxane, benzene, and most other organic solvents. The polyquaternary is stable to heat, alkali, and drying. Analysis of a dried sample (corrected for water content by Karl Fischer determination) is C 66.7%, H 8.52%, Cl 16.45%, N 6.56%; calculated for $(C_{12}H_{18}NCl)_x$, C 68.1%, H 8.57%, Cl 16.75%, N 6.62%. The sulfonium polymer, on the other hand, is decomposed by strong alkali and strong nucleophiles, by heat (at 95° in dilute aqueous solution), and upon drying,

even at Dry Ice temperatures.

The viscosities of dilute aqueous solutions of dialyzed poly(trimethyl(ar-vinylbenzyl)ammonium chloride) are highly sensitive to small amounts of crosslinking or transfer agents present at the time of polymerization (Table I).

TABLE I
Specific Viscosities of Aqueous Solutions of Poly(trimethyl (ar-vinylbenzyl)ammonium chloride)

Polymer from PVBC polymerized with	Specific viscosity (25°)	
	at 0.500%	at 0.0625%
0.30% DDM[a]	1.738	0.494
0.10% DDM[a]	1.858	0.531
0.050% DDM[a]	2.837	0.792
—	3.017	0.834
0.050% DVB[b]	12.472	2.297
0.10% DVB[b]	22.501	2.489
0.20% DVB[b]	19.381	1.207
0.40% DVB[b]	7.73	0.496

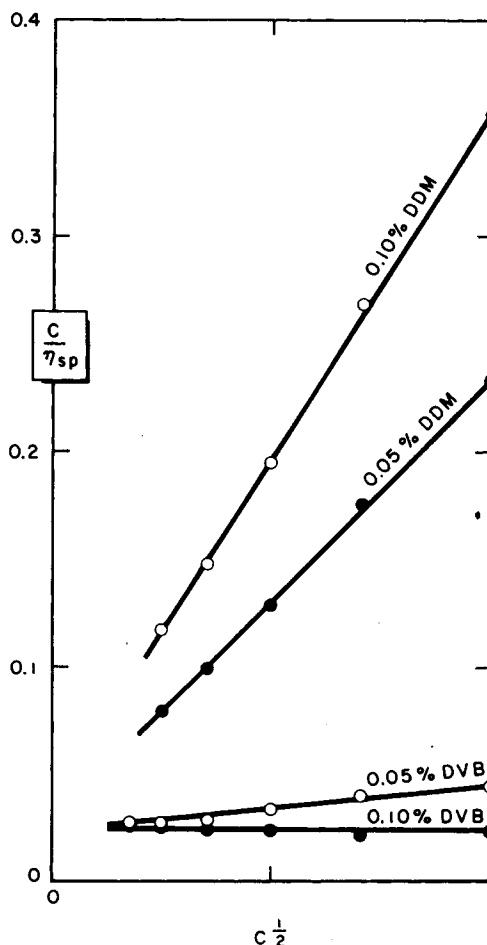[a] tert-Dodecyl mercaptan.
[b] m-Divinylbenzene.

Fig. 1. Fuoss plot of viscosities of linear and microgel poly(trimethyl(ar-vinylbenzyl)ammonium chloride)s. $c =$ polymer concentration in g./100 ml. deionized water.

The transition from linear polyelectrolyte to microgel polyelectrolyte is shown by a Fuoss plot of solution viscosities (Fig. 1). The ratio η_{sp}/c falls with increasing concentration for linear polymers and for those containing less than 0.10% divinylbenzene, and increases with increasing concentration for the swollen-sphere structures formed with 0.10% or more divinylbenzene.

Current studies, to be reported soon, are directed to the effects of nucleophile structure upon reactivity with PVBC, and to the kinetic character of these displacement reactions.

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Fig. 1. Inflexion des courbes η_{sp}/c par rapport à c pour la polystyrène dans divers solvants, à de faibles concentrations (Streeter et Boyer[2]).

Anomalie de la Viscosite des Solutions de Polyisoprene cis-1,4 à de Faibles Concentrations

Le comportement des solutions de composés macromoléculaires, à de faibles concentrations, a été l'objet de nombreuses études.[1] Il y est question d'une concentration critique, c'est à dire d'une concentration au-dessous de laquelle les macromolecules ont la possibilité de se mouvoir de façon indépendante, la distance moyenne entre les molécules étant supérieure à leurs dimensions.

On a observé des anomalies dans la viscosité des solutions aux alentours de la concentration critique: la courbe η_{sp}/c par rapport à c, présente une inflexion aux faibles concentrations[2] (Fig. 1a) pour marquer ensuite, aux concentrations encore plus faibles, une croissance jusqu'à un certain point au delà duquel elle décroît à nouveau[2] (Fig. 1b).

Les anomalies de la viscosité des solutions de composés macromoléculaires ont été observées lors des déterminations de viscosité à l'aide de viscosimètres capillaires. Elles ont été expliquées, dans la plupart des cas, par l'adsorption du polymère sur les parois du capillaire, qui peut avoir deux effets: Le premier, le plus marqué, est celui qui conduit à une diminution de 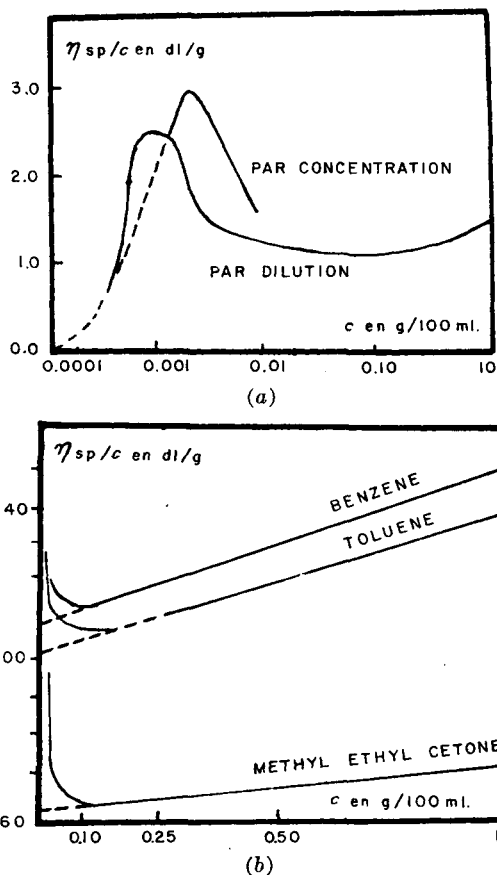la concentration de la solution, accompagnée d'une diminution correspondante du temps de chute. L'autre effet change plus la forme de la courbe η_{sp}/c aux faibles concentrations et est provoqué par la diminution du rayon du capillaire, due à la pellicule adsorbée. Si r est le rayon du capillaire et a l'épaisseur de la pellicule adsorbée, nous avons:[3]

$$\eta_{rel} = \eta_{rel}* \left(\frac{r-a}{r}\right)^4$$

ou

$$\eta_{sp}*/c = \eta_{sp}/c + 4a/rc\,(\eta_{sp}/c + 1)$$

qui, pour η_{rel} il peut s'écrire avec approximation:

$$\eta_{sp}*/c = \eta_{sp}/c + 4a/rc$$

où η et $\eta*$ sont les viscosités vraies, respectivement celles qui ont été observées.

Pour des concentrations faibles, la valeur de c du dénominateur fait que la valeur du terme de correction soit plus grande et donc que les valeurs $\eta_{sp}*/c$ soient plus grandes que les valeurs de η_{sp}/c vraies.

Au cours de l'étude des poids moléculaires des solutions de polyisoprène cis-1,4 à l'aide de la méthode viscosimétrique,[4,5] en utilisant un viscosimètre Höppler à bille, nous avons observé que la représentation graphique des courbes η_{sp}/c par rapport à c présentait une inflexion pour