Properties

Solution Properties of Poly(N-Butyl Methacrylamide)

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Summary
      Dilute solutions of poly(N-butyl methacrylamide) in
methanol, dimethylformamide, and cyclohexanone were in-
vestigated by light scattering, osmometry and viscometry.
From the intrinsic viscosity data, the characteristic ratio,
$C_\infty = 9.9$, was estimated. This value is compared with those
for other N-substituted polyacrylamides.

      In this paper we report on the solution properties of
poly(N-butyl methacrylamide) (PBMAm) prepared by radical-initi-
ated polymerization, namely, its solubility, determination of
the molecular weight by light scattering and osmometry, cor-
relation of the intrinsic viscosity with the molecular weight,
and the configurational characteristics of the chain.

Experimental
      Monomer: N-Butyl methacrylamide was prepared by a re-
action of 2.2 moles of butylamine with 1 mole of methacroyl
chloride in benzene solution at -5 °C. After removal of
butylamine hydrochloride and evaporation of benzene from the
reaction mixture, the monomer was distilled with Cu_2Cl_2 as
inhibitor. It was purified by rectification on a 0.5 m column
packed with stainless steel coils. Yield 70 %, b.p. 72 °C
(66 Pa), ρ_{25} = 0.9213 g/cm^3, purity better than 99.9 %. Purity
of the monomer was determined with an F-11 Perkin-Elmer gas
chromatograph (columns 10 % Apiezon with Chromosorb W and
Octoil S).
Solvents were purified by standard procedures.
Polymerization was carried out in sealed ampoules at 60 ± 0.2 °C
with dimethyl sulphoxide as solvent and $\alpha,\alpha^{'}$-azobis(iso-
butyronitrile) (Lachema Brno, recrystallized three times from
ethanol) as initiator. Dissolved oxygen was removed from the
polymerization mixture by triple evacuation (in each cycle,
pressure was balanced with catalytically purified nitrogen).
Polymers were precipitated into dry diethyl ether. Polymer
samples differing in molecular weight were obtained by
changing the concentrations of the initiator (from 2×10^{-6} to
1×10^{-5} mol/cm^3) and monomer (from 2×10^{-3} to 5×10^{-3} mole/cm^3)
in the polymerization mixture.
Fractionation. Two PBMAm samples were fractionated at 25 °C

by successive precipitation from solutions in an acetone-methanol mixture (9:1, by volume) with water as precipitant. The initial polymer concentration was about 1 % by weight.Dissolution, which was very slow and incomplete at 25 °C (particularly with sample 7), was accomplished by heating to 40-50 °C for about one hour. The precipitation was performed in the usual way and the fractions settled as transparent or slightly opalescent viscous liquids. They were precipitated into water, and dried in vacuo at 40 °C. In this way, samples 1 and 7 were divided into 5 and 4 primary fractions, respectively (1/1 to 1/5; 7/1 to 7/4). The fractions were further subdivided into four and three secondary fractions, respectively (1/1-1 to 1/1-4; 7/1-1 to 7/1-3).

As shown by Table 1, the polydispersity of fractions was rather high, the index M_w/M_n ranging from 1.3 to 1.8. The M_w/M_n values for non-fractionated samples were 2.3 to 4.

Table 1: Results of measurements of poly(N-butyl methacrylamide) samples

Sample	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	$[\eta]$, cm^3/g, at 25 °C	
			methanol	cyclohexanone
Non-fractionated samples				
1	63[a]	–	18.5	10.0
2	82	25	21.4	–
3	131	35	30.2	–
4	177	60	40.9	–
5	213	90	35.5	–
6	550	330	72.8	–
7	200[a]	–	40.0	–
Fractions				
1/5	21[a]	–	8.1	7.1
1/4	40.7	27	12.3	9.3
1/1-4	77	40	20.9	11.1
1/2	88	62	23.2	11.9
1/1-1	143	103	30.6	–
7/2	210	146	43.1	–
7/1-3	222	125	43.3	17.6
7/1-2	425	–	70.3	22.5

[a] M_η, calculated from $[\eta]$ in methanol.

Light scattering. The weight-average molecular weights, M_w, were measured with a commercial Fica 40 apparatus in vertically polarized light, wavelength 546 nm, angular range 30-150 °, temperature 25 °C. The apparatus was calibrated with a benzene standard (absolute scattering value at 90 °C 21.8x10^{-6} cm^{-1}). The refractive index increment of PBMAm in dimethylformamide solution (dn/dc = 0.079 cm^{3}g^{-1}) was measured with a Brice-Phoenix differential refractometer. Experimental data from five concentrations were treated by the Zimm extrapolation method.

Osmometry. An automatic membrane osmometer Knauer was used
with methanol as solvent at 30 °C. The number-average mole-
cular weights, M_n, were calculated from the reduced osmotic
pressure extrapolated to zero concentration.
Viscometry. Viscosities were measured in capillary Ubbelohde
viscometers adapted for dilution. The intrinsic viscosities
were determined by extrapolation from measurements at 4 or
5 concentrations. No corrections for the kinetic energy loss,
draining, and the shear-rate effects were necessary.

RESULTS AND DISCUSSION

Poly(N-butyl methacrylamide) is soluble in alcohols,
dimethyl formamide, and dimethyl sulfoxide. It is not dis-
solved by esters, lactones, nitriles, and by non-polar liquids
such as hydrocarbons. Fractions of PBMAm of molecular weight
lower than 0.5×10^6 are dissolved by cyclohexanone on prolonged
heating to 60 °C and do not precipitate on cooling to 25 °C.
Samples of higher molecular weights are only partly soluble,
probably because of a high-molecular-weight tail.
The logarithmic dependences of the intrinsic viscosity,
[η], on the molecular weight, M_w, (Table 1) are linear for
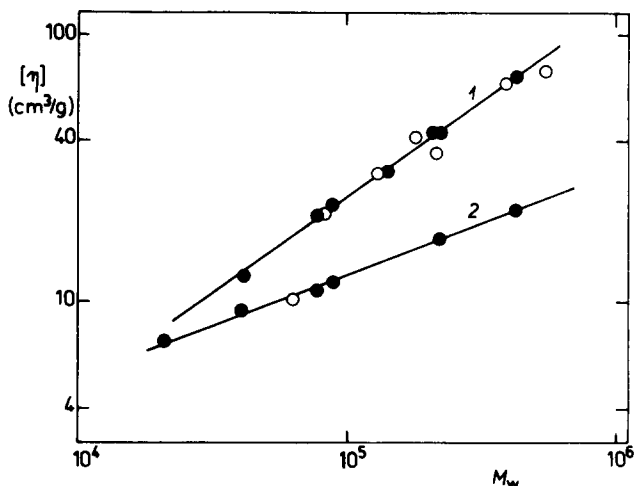both methanol and cyclohexanone at 25 °C (Fig.1), and the

Fig.1 Dependence of the intrinsic viscosity on the molecular
weight for poly(N-butyl methacrylamide) at 25 °C
1 Methanol, 2 cyclohexanone. Fractions ● , non-frac-
tionated samples ○ .

parameters of the Mark-Houwink-Kuhn-Sakurada equation,

$$[\eta] = K \, M^a \qquad , \qquad (1)$$

are $K = 6.21 \times 10^{-3}$ and 0.165, a = 0.72 and 0.37_5 for methanol
and cyclohexanone, respectively. For reasons mentioned above,
the dependence for cyclohexanone should not be extrapolated
much beyond $M \simeq 0.5 \times 10^6$.

The analysis of the intrinsic viscosity data is based on the following equations (1)

$$[\eta]/M^{1/2} = K_O + 0.346 \, \Phi_O \, B \, M^{1/2} \tag{2}$$

$$K_O = \Phi_O \, (\overline{R_O^2}/M)_\infty \quad , \tag{3}$$

$$C_\infty \equiv (\overline{R_O^2}/nl^2)_\infty = (\overline{R_O^2}/M)_\infty (M_O/2l^2) . \tag{4}$$

Here, Φ_O is the Flory viscosity parameter ($\Phi_O = 2.6 \times 10^{23}$ (1) for $\overline{R_O^2}$ in cm^2 and $[\eta]$ in cm^3/g), M_O is the molecular weight per repeating chain unit ($M_O = 141$ for PBMAm), $\overline{R_O^2}$ is the mean-square end-to-end distance for a chain comprising n main chain bonds each of length l (l = 1.53×10^{-8} cm for a C-C single bonds (1)) and unperturbed by the excluded-volume effect, nl^2 is the corresponding quantity for the freely jointed chain, B is the polymer-solvent interaction parameter, and C_∞ is the characteristic ratio. It is assumed that n is large enough for the chain to be in the random-coil configuration.

The Stockmayer-Fixman-Burchard plots, $[\eta]/M^{1/2}$ vs. $M^{1/2}$, are linear for both methanol and cyclohexanone (Fig.2) so that the determination of the viscosity constant K_O by extrapolation to $M^{1/2} = 0$ is not difficult. The intercepts are
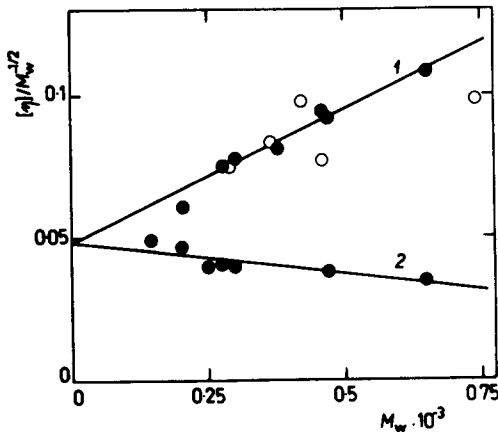

Fig.2   The Stockmayer-Fixman-Burchard plot of data for poly(N-butyl methacrylamide) at 25 °C
Notation of points as in Fig.1.

almost identical ($K_O = 0.049$). According to the slopes of these plots, methanol is a good solvent (B > 0) and cyclohexanone is a poor one (B < 0). This can explain the limited solubility of the polymer in cyclohexanone at high molecular weights. From K_O we obtain, by means of eqns (3) and (4), $(\overline{R_O^2}/M)_\infty = 0.33 \times 10^{-16}$ and $C_\infty = 9.9$.

In Fig.3 the values of C_∞ for N-substituted derivatives of polymethacrylamide are correlated with the approximate molar volumes of the chain repeating unit, V_x. These have been calculated from the additive van-der-Waals volume contributions of atomic groups tabulated by van Krevelen (2). They serve as an approximate measure of the bulkiness of the substituents.
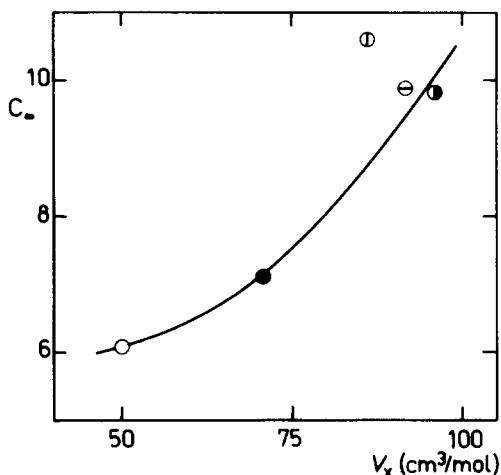

Fig.3   Plot of the characteristic ratio C_∞ against the molar volume of the chain repeat unit V_x of N-substituted polymethacrylamide.
Chain repeat unit $CH_2C(CH_3)CONHR$ with $R:H$ [4] $\bigcirc$, C_2H_5 [5] ●,
$CH_2CH(OH)CH_3$ [6] ⊕, C_4H_9 (this paper) ⊖, C_6H_5 [3] ◐.

Kurata and Stockmayer (3) found good correlation of C_∞ with V_x for other polymers differing only in the size of the side groups.
   For the derivatives of polymethacrylamide (Fig.3), the correlation of C_∞ with V_x is smooth, with only the point for poly[N(2-hydroxypropyl methacrylamide)] lying above the curve for the other polymers. This fact may indicate that the effect of polar group on the chain conformation, though not negligible, is yet less important than the steric repulsion of the $-CH_2CH(OH)-CH_3$ groups.

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