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Abstract

Full Text

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DETERMINATION OF THE MOLECULAR WEIGHT OF CHELATE POLYMERS

Chelate compounds are formed in those cases when the molecule of an organic substance reacting with a metal ion contains, as a rule, two donor groups and is capable of forming a metallocycle. If one molecule of an organic compound contains at least two pairs of donor groups, then in some cases the metal ion can form repeatedly recurring metallocycles, which are called chelate units. The high-molecular compounds arising in this way have been given the name chelate polymers. As a rule, these compounds are solid substances, infusible and insoluble. Thus, determination of their molecular weight is a difficult problem.

Attempts at even a rough estimate of the molecular weight of polychelates have been made previously. Marvel and Tarkoy ([1]) described several metal polymers with Schiff bases of 5,5 -methylene-bis-salicylaldehyde and *o*-phenylenediamine. Measuring the viscosity of the polymeric Schiff base, the authors found its degree of polymerization to be $n = 45$, assuming that the polychelate has the same value of n.

V. V. Korshak et al. ([2–5]) estimate the molecular weight of metal polymers with various bis- -diketones on the basis of analytical results. By this method the degrees of polymerization were determined; depending on the structure of the polymers, they varied from 2 to 23. The molecular weight, correspondingly, did not exceed 8000–10000.

It is known that chelate polymers can contain three types of terminal groups in the macromolecule:

$$\mathrm{HLgn}\left[-\mathrm{M}-\mathrm{Lgn}-\right]_n \mathrm{M}-\mathrm{LgnH} \tag{1}$$

$$\mathrm{HLgn}\left[-\mathrm{M}-\mathrm{Lgn}-\right]_n \mathrm{M}-\mathrm{A} \tag{2}$$

$$\mathrm{A}\left[-\mathrm{M}-\mathrm{Lgn}-\right]_n \mathrm{M}-\mathrm{A} \tag{3}$$

where H is a hydrogen atom, H_2Lgn is a ligand molecule containing 4 (or more) donor atoms, M is a divalent metal ion, and A is a monovalent anion.

Depending on the conditions under which the polycondensation reaction is carried out, it is possible to obtain polychelates with different terminal groups. With an excess of metal salt we can obtain anionic groups at the ends of the macromolecules. The amount of these groups (in percent) in the polymer will be (for case (3)):

$$A = \frac{M_{2A}}{M_{\text{pol}}} \cdot 100; \qquad M_{\text{pol}} = \frac{M_{2A}}{A} \cdot 100.$$

We determined the molecular weight of the polymers obtained using the radioactive-tracer method.

As the object of investigation we chose the chelate polymers, described by us earlier [5,9], of the following structures:

[[chemical structural formula of polymer (I), with terminal Br—Cu groups and repeating chelate units]]

(I)

where $R = 2H-$, $-(CH_2)_2-$, $-(CH_2)_6-$ and o-C_6H_4-

[[chemical structural formula of polymer (II), with terminal Br—Cu groups and repeating chelate units]]

(II)

[[chemical structural formula of polymer (III), with terminal Br—Cu groups and thiazole-containing chelate u

(III)

where $R = H-$ and CH_3-.

In all cases the synthesis of the polymers was carried out with cupric bromide labeled with the radioactive isotope Br^{82}. The radiation of this isotope is easily recorded, and its half-life (36 h) is convenient for carrying out the work.

Table 1

Molecular weight and degree of polymerization of chelate polymers

Polymer	Br^{82}, %	Relative error, %	Mol. wt.	Degree of polym.
(I) $R = 2H-$	0.30 ± 0.03	10.0	53 500	168

Polymer	Br^{82}, %	Relative error, %	Mol. wt.	Degree of polym.
(I) $R = -(CH_2)_2-$	0.21 ± 0.03	14.3	76 400	222
(I) $R = -(CH_2)_6-$	0.25 ± 0.03	11.9	64 000	160
(I) $R = o\text{-}C_6H_4-$	0.39 ± 0.03	7.7	41 100	105
(II)	0.23 ± 0.03	13.0	69 500	216
(III) $R = H-$	0.38 ± 0.03	7.9	42 100	86
(III) $R = CH_3-$	0.45 ± 0.04	8.9	35 600	71

Table 1 gives the molecular weights and degrees of polymerization of the chelate polymers, calculated by formula (2), where the percentage of anion (A) was calculated as the ratio of the fraction of the activity of Br^{82} in the precipitate to the activity introduced. The molecular-weight values found by us lie in the range 36 000–77 000, which is 3–4 times higher than the values reported by other authors [1–5].

The molecular weight of polymers of structure (III) is somewhat lower than that of polychelates of structures (I) and (II). This is apparently connected with the different degree of stability of the chelate unit in the macrochain.

Among polymers of structure (I), the magnitude of the molecular weight varies depending on the value of R. We assumed that this is connected with the differing ease of oxidation of the amines participating in the reaction. The more readily the amine is oxidized, the sooner chain scission occurs and the lower the molecular weight of the polymer. But the process of oxidation of amines also proceeds in their solutions on standing. Consequently, with an increase in the time between preparation of the solution of an easily oxidized amine and its use in the reaction, the molecular weight of the polychelate should decrease. Such amines

in our polymers were hexamethylenediamine ((I) $R = -(CH_2)_6-$) and o-phenylenediamine ((I) $R = o\text{-}C_6H_4-$). The investigations carried out confirmed our supposition (see Table 2).

Table 2

Dependence of the molecular weight and polymerization coefficient of certain chelate polymers on the standing time of the initial amine solutions

Amine	Polymer	Standing time of solution	Br^{82}, %	Relative error, %	Mol. wt.	Coeff. of polym.
Hexamethylenediamine	(I) $R = -(CH_2)_6-$	5–15 min.	0.25 ± 0.03	11.9	64 000	160
Hexamethylenediamine	(I) $R = -(CH_2)_6-$	3–5 hr.	0.44 ± 0.04	9.1	36 400	91
Hexamethylenediamine	(I) $R = -(CH_2)_6-$	2 days	6.53 ± 0.15	2.3	2440	6.1
o-Phenylenediamine	(I) $R = o\text{-}C_6H_4-$	5–15 min.	0.39 ± 0.03	7.7	41 100	105
o-Phenylenediamine	(I) $R = o\text{-}C_6H_4-$	3–5 hr.	0.75 ± 0.02	2.7	21 200	54
o-Phenylenediamine	(I) $R = o\text{-}C_6H_4-$	2 days	10.4 ± 0.15	1.4	1530	3.9

When the reaction was carried out with a freshly prepared amine solution, we obtained the maximum values of the molecular weights. When the standing time of the amine was increased to 3–5 hr, the molecular weight of the polymers fell by approximately a factor of 2. Keeping the amine solutions for 2 days or more leads to the formation of low-molecular-weight compounds.

It is interesting to note that, when the solution of *o*-phenylenediamine was allowed to stand before the reaction for 3–5 hr, the molecular-weight value of the polymer obtained ((I) $R = o\text{-}C_6H_4-$) agrees well with the data of the American authors ([1]).

In the case of other structures ((I) $R = 2H-$; (I) $R = -(CH_2)_2-$), the molecular weight of the polymers does not change when the amine solutions are allowed to stand for 2 days.

Polymers of structure (I) can be obtained both by the nascent-reagents method and starting from polymeric Schiff bases ([6]). As our investigations have shown, the method of synthesis of such polymers has practically no effect on the value of the number-average molecular weight. The discrepancies in the values found always lie within the relative errors of the experiments.

It was also necessary to determine whether, under these conditions, binding of bromine anions occurs on the surface of the polymers obtained. Such a side process would lead to underestimated true values of the molecular weights of the polychelates. For this purpose we completely reproduced the method for determining molecular weight on a monomeric compound of analogous structure –copper salicylalethylenediimine:

[structural formula]

in which bromine anions theoretically should not be present. We established that

the copper complex contains no radioactive bromine, i.e., binding was absent.

The method we have found for determining the molecular weight of insoluble and infusible chelate polymers gives stable, reproducible results.

Experimental Part

Synthesis of chelate polymers and measurement of activity. The polymers were synthesized by methods described by us earlier ([6–9]). Aqueous solutions were used as the solution of the metal salt—

copper bromide labeled with the radioactive isotope Br^{82}. The activity of Br^{82} was counted with a scintillation counter with a NaJ/Tl single crystal measuring 40×60 mm; an aluminum cup containing the filters with the dried precipitates was placed on the holder of the counter. The activities obtained were corrected for decay of the isotope Br^{82}.

Determination of the initial activity of copper bromide. To a measured volume of an aqueous solution of copper bromide containing the radioactive isotope Br^{82}, an excess of silver nitrate solution was added. The precipitated silver bromide was filtered off, washed with water, and its activity was measured by the procedure described above.

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Note: Figure translations are in progress. See original paper for figures.