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Potentiometric determination of the molecular weight of polymers

A. S. Saraç*, B. Ustamehmetoğlu, and C. Erbil

Department of Chemistry, Istanbul Technical University, Maslak, TR-80626 Istanbul, Turkey

SUMMARY

The determination of acid end-groups of acrylamide and acrylonitrile polymers initiated by cerium (IV)-malonic acid, cerium (IV)-tartaric acid and cerium (IV)-citric acid redox initiators systems was made in aqueous and nonaqueous media potentiometrically. The effect of solvent, titrant and electrode system on the half-neutralization potentials and number-average molecular weights, $\overline{M_n}$, were determined potentiometrically and were studied. These $\overline{M_n}$ values were compared with those obtained by viscosimetric and conductometric methods.

INTRODUCTION

Quantitative determination of end functional groups is particularly difficult because of the extremely low level at which they exist in the polymer. A quantitative measure of functional groups in polymers gives important clues about the conformation of functional polymers, molecular weight and polymerization mechanism(1-3).

To obtain acrylonitrile and acrylamide polymers containing functional end-groups, cerium (IV)-hydroxycarboxylic acid and polyaminocarboxylic acid redox systems have been recently used in our laboratory (4-6). In this work, a procedure was described whereby acidic groups in polymers at the microequivalent level may be measured by aqueous and nonaqueous titrations. The determination of acid end-groups of polyacrylamides and polyacrylonitriles initiated by cerium (IV)-malonic acid, cerium (IV)-tartaric acid and cerium (IV)-citric acid redox systems was made potentiometrically by using aqueous NaOH, alcoholic NaOH (C_2H_5OH-NaOH) and tetrabutylammonium hydroxide in isopropyl alcohol : toluene (1:9) as titrant.

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*Corresponding author

EXPERIMENTAL PART

a) Materials

Ethylene glycol (EG), malonic acid (MA), tartaric acid (TA), citric acid (CA), acrylamide (AM), acrylonitrile (AN), dimethylformamide (DMF) and tetrabutylammonium hydroxide ($TBuNH_4OH$) were purchased from the Merck Co. and used without further purification.

b) Potentiometric Titrations

Glass-modified calomel electrode (by potassium chloride in methanol) system was used for potentiometric titrations. Electrodes were equilibrated in the solvent when not in use. They were calibrated with aqueous buffer solutions and pH measurements were standardized in water-organic solvent mixtures as described by Mussini et al. (7). All titrations were performed with a Metrohm E-576 potentiograph. The studies were carried out at 25°C and titration solutions were agitated with a magnetic stirrer. The potentiometric data (added volume of titrant, mV of the solution) were collected by using the automated titration system.

The procedures for polymerizations and viscosimetric measurements were similar to those reported earlier(4-6).

Typical titration curves and the results obtained are given in Figure 1, and Tables 1a and 1b.

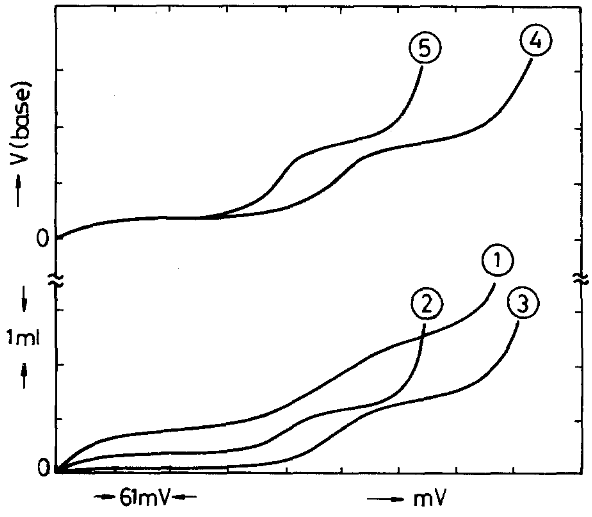

Fig.I. Titration curves for ① MA-AM/EG-H_2O/glass-calomel/$TBuNH_4OH$;② MA-AM/H_2O/glass calomel/NaOH ;③ MA-AM/H_2O/Pt-glass/NaOH ;④ CA-AM/H_2O/Pt-glass/NaOH;⑤ CA-AM/H_2O/glass-calomel/NaOH

Table Ia. $\overline{M}_n$, $\overline{M}_v$ and HNP values for Malonic acid and related polymers

Sample No	Sample and corresponding weight (g)	Solvent-Titrant-Electrode Matching	HNP values	Viscosimetric Molecular Weight, $\overline{M}_v$	Potentiometric Molecular Weight, $\overline{M}_n$
1	MA, 0.05	H_2O/**NaOH**/glass-calomel	373	-	105, 104. 06*
2	MA, 0.05	H_2O/**NaOH**/Pt-glass	382	-	107
3	MA, 0.05	EG+H_2O/**$TBuNH_4OH$**/glass-calomel	127	-	106
4	MA-AM, 0.05	H_2O/**NaOH**/glass-calomel	300	3100	1670
5	MA-AM, 0.05	H_2O/**NaOH**/Pt-glass	375	3100	1540
6	MA-AM, 0.10	EG+H_2O/**$TBuNH_4OH$**/glass-calomel	375	3100	1670
7	MA-AM, 0.14	EG/**$TBuNH_4OH$**/glass-calomel	307	9600	6400
8a	MA-AN, 0.25	DMF/**C_2H_5OH-NaOH**/glass-calomel	288	17400	4000
8b	MA-AN, 0.25	EC+PC/**C_2H_5OH-NaOH**/Pt-Pt	-	17400	16700**
9a	MA-AM, 0.05	H_2O/**NaOH**/glass-calomel	352	2700	2200
9b	MA-AM, 0.05	H_2O/**NaOH**/Pt-glass	-	2700	2400**

Table Ib. $\overline{M}_n$, $\overline{M}_v$ and HNP values for Citric and Tartaric acids, and related polymers

Sample No	Sample and corresponding weight (g)	Solvent-Titrant-Electrode Matching	HNP values	Viscosimetric Molecular Weight, $\overline{M}_v$	Potentiometric Molecular Weight, $\overline{M}_n$
10	CA, 0.05	H_2O/**NaOH**/glass-calomel	360	-	210, 210*
11	CA, 0.05	H_2O/**NaOH**/Pt-glass	345	-	211
12	CA, 0.05	EG+H_2O/TBuNH_4OH/glass-calomel	397	-	208
13	CA-AM 0.1	EG/TBuNH_4OH/glass-calomel	265	27300	6800
14	CA-AM, 0.05	H_2O/**NaOH**/Pt-glass	390	6800	1500
15	CA-AM, 0.05	H_2O/**NaOH**/glass-calomel	315	6800	1770
16	CA-AN, 0.25	DMF/**TBuNH_4OH**/glass-calomel	232	15.000	3750
17	TA, 0.05	H_2O/**NaOH**/glass calomel	322	-	153
18	TA, 0.05	EG+H_2O/**TBuNH_4OH**/glass-calomel	337	-	153
19a	TA-AM, 0.05	H_2O/**NaOH**/glass-calomel	322	1250	1100
19b	TA-AM, 0.05	H_2O/**NaOH**/Pt-Pt	-	1250	1600**
20a	TA-AN, 0.25	DMF/**C_2H_5OH-NaOH**/glass-calomel	253	11000	7100
20b	TA-AN, 0.25	EC+PC/**C_2H_5OH-NaOH**/Pt-Pt	-	11000	11400**
20c	TA-AN, 0.25	DMF/**C_2H_5OH-NaOH**/Pt-Pt	-	11000	11800**
21	TA-AM, 0.05	H_2O/**NaOH**/glass-calomel	352	23000	1250
22	TA-AM 0.05	EG+H_2O/**TBuNH_4OH**/glass-calomel	345	23000	1430

* Theoritical molecular weights.

** Conductometric results of the same polymers(6).

RESULTS and DISCUSSION

Different half-neutralization potential (HNP) values were observed for different electrode systems such as Pt-glass and glass-calomel as expected and the effect of solvent on HNP is also obvious from Fig 1.

Although the potentiometric determination method in nonaqueous media by glass-calomel electrode system is suitable for acids and bases (8,9) Pt-glass and glass-calomel electrode systems give similar results in respect to M_n values of low molecular weight polymers. No comparable results were observed with the viscosity-average molecular weights at high molecular weight products (Tables 1a, 1b). Furthermore, good correlation was obtained with M_n and M_v for high molecular weight of AN polymers by the conductometric method(6) rather than potentiometric results (i.e. 8 and 20 no. exps.). A comparison of these systems shows that the use of an appropriate electrode permits titration of acid end-groups in polymers and avoids the problem of alkali metal poisoning encountered with glass-calomel electrodes.

REFERENCES

1. Waltz,J.E. and Taylor,G.B., (1947) Anal.Chem. 19, 448.
2. Kirby,J.R. and Baldwin,A.J., (1968) Anal.Chem. 40, 689.
3. Morcellet,M. and Wozniak,M., (1991) Macromolecules 24, 745.
4. Saraç,A.S., Erbil,C. and Soydan,A.B., (1992) J.Appl.Polym.Sci. 44, 877.
5. Erbil,C., Cin,C., Soydan,A.B. and Saraç,A.S., (1993) J.Appl. Polym.Sci. 47, 1643.
6. Erbil,C., Ustamehmetoğlu,B., Uzelli,G. and Saraç,A.S. (in press) Europ.Polym.J.
7. Mussini,T., Covington,A.K., Longhi,P. and Rondinini,S. (1985) Pure & Appl.Chem. 57, 866.
8. Miron,R.R. and Hercules, D.M., (1961) Anal.Chem. 33, 1771.
9. Önen,A. and Saraç,A.S., (1990), J.Anal. and Appl. Pyrolysis 17, 227.

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