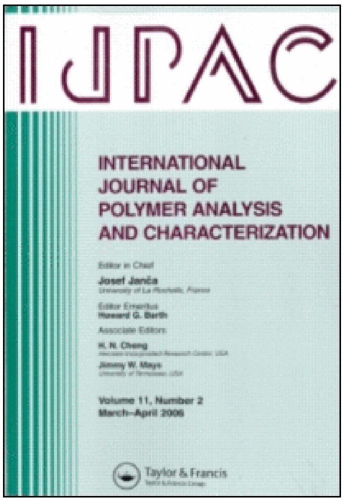

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Chemical Polymerization of Acrylamide Initiated with Ce(IV)-Dicarboxylic Acid Redox System: Effect of Chain Length Between the Carboxyl Groups

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Aqueous polymerization of acrylamide (AAm) was carried out with the Ce(IV)-dicarboxylic acid initiator system. Dicarboxylic acids with numbers of methylene groups ranging from 1 to 7 were used to elucidate the effect of chain length between the carboxyl groups on the formation of polymer, which is reflected in yield and molecular weight of polymer. The end group analysis of polyacrylamides was carried out by using conductometric titration. The number average molecular weight results from end group analysis are compared with values from viscometric analysis.

Keywords: Polycrylamide; Chemical polymerization; Dicarboxylic acid

Polyacrylamide (PAAm) has been the focus of many studies because of its solubility in water and ease of synthesis of functional end groups. Ceric salts[1,2] or ceric salt-reducing agent systems in aqueous acidic solution are used as initiators of vinyl polymerization. The reducing agents used with Ce(IV) are glycol[3], alcohols[4,5], ketones[6], aldehydes[7], and amino[8] and polyminocarboxylic acids[9–12]. The same systems were

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also used for the graft copolymerization of acrylonitrile and acrylamide[13] and synthesis of block copolymer of ketonic resin-polyacrylonitrile[14].

Electrochemical initiation has also been used successfully for the polmerization of acrylamide (AAm)[15–17] and acrylonitrile[18]. Recently polymerization of AAm was investigated in aqueous solution in the presence of Ce(IV) salt–oxalic acid initiator system in an electrochemical cell with separation of anolyte and catholyte[19].

However, initiation by dicarboxylic acid has not been investigated in detail, even though the electrochemical polymerization of dicarboxylic acid has been found to be effected by the chain length between the carboxyl groups[20,21], which is reflected in the properties of the polymers (i.e., melting point, activation energies of decomposition of acids, cyclic intermolecular hydrogen bondings, and formation polymer)[22,23]. Here we report the chemical polymerization of AAm initiated with oxalic, malonic, adipic, pimelic, suberic, and azealinic acids in the presence of Ce(IV) and some properties of PAAm obtained depending on whether the acids contain an even or odd number of methyl groups.

EXPERIMENTAL

Materials

Acrylamide, $(NH_4)_2[Ce(NO_3)_6]$, HNO_3, NaOH, and dicarboxylic acids were all Merck reagent grad chemicals of the highest purity and were used without further purification. Dicarboxylic acids; oxalic acid (OA), malonic acid (MA), adipic acid (AA), pimelic acid (PA), suberic acid (SA), and azealinic acid (AzA) used in this study have general formula of $HOOC{-}(CH_2)_n{-}COOH$ where $n = 0$ for oxalic acid $n = 1$ for malonic acid, $n = 4$ for adipic acid, $n = 5$ for pimelic acid, $n = 6$ for suberic acid, and $n = 7$ for azealinic acid.

Polymerization Procedure

Cerium salt was dissolved in water in the presence of nitric acid and slowly added to the monomer and reducing agent solution mixture at room temperature (30°C) and mixed continuously during the reaction period (1 h).

After a certain period of polymerization (1 h), the contents of the flask were poured into acetone in order to precipitate the polyacrylamide. The precipitate was filtered, washed with acetone several times, and dried at room temperature. The molecular weights of the polymers were determined using an Oswald viscometer at 30°C and were calculated from the

TABLE I Number Average Molecular Weight Estimated by End Group Determination

Polyacrylamide with functional end groups	n	Dicarboxylic acid, M	End group number	$M_v \times 10^{-3}$*	Yield %	$M_n \times 10^{-3}$**
MA-AAm	1	1×10^{-2}	4	124	85.00	37
		8×10^{-3}		30	24.10	18
AA-AAm	4	4.57×10^{-2}	4	84	4.40	23
		8×10^{-3}		16	9.12	11
PA-AAm	5	5.7×10^{-2}	4	63	100.00	15
		8×10^{-3}		19	27.85	7
SA-AAm	6	6×10^{-2}	4	138	6.63	37
		8×10^{-3}		31	17.06	17
AzA-Aam	7	8×10^{-2}	4	109	24.96	20
		8×10^{-3}		6	1.00	10

n = number of $-CH_2-$ groups.

*Molecular weight calculated from the intrinsic viscosity measurement.

**Number average molecular weight obtained by conductometric determination for polyacrylamide $[\eta] = 6.80\ 10^{-4} M_n^{0.66}$.

Polymerization reaction period = 1 h, Temperature = 30°C, Monomer cencentration = 0.77 mol/It, $[Ce(IV)] = 5 \times 10^{-3}$ for MA and 1×10^{-2} for AA, PA, SA and AzA, $n = CH_2$ number.

[Yield % = (Weighted polymer/monomer) × 100].

viscosity data by using the following Mark–Houwink equation for aqueous solutions (1):[24]

$$[\eta] = 6.80\ 10^{-4}\ M_n^{0.66}\ \mathrm{dLg}^{-1} \qquad (1)$$

where $[\eta]$ and M_n* are intrinsic viscosity and molecular weight calculated from the intrinsic viscosity measurement (which is given as M_v in Table I) respectively.

Since the electrochemical polymerization of dicarboxylic acids is known[20,21], in order to eliminate the possible polymerization of these acids by ceric(IV) ammonium nitrate (CAN) under our conditions, blank experiments that gave no product were done in which monomer was excluded. Blank experiments from which Ce(IV) and dicarboxylic acids were excluded also gave no detectable polymerization during the same reaction time. These indicate that the reaction between Ce(IV) and dicarboxylic acids can initiate the acrylamide polymerization.

*since the method used for obtaining the constants in Eq. (1) yields M_n.

The procedure used for the conductometric titrations consisted of dissolving carboxylic acids and polymers in 20 ml of the solvent and titrating with ca. 0.1 N titrant. The conductometric titrations were carried out in a glass cell kept at a constant temperature of 25°C. For each titration experiment, the cell was filled with 20 ml solvent in which a known amount of solid polymer was dispersed by magnetic stirring. The polymer completely dissolved within a few hours. The polymer solution was then titrated with 0.1 N titrant added from a microbiuret. Blank titrations were carried out for each solvent.

The conductivities are plotted versus milliliters of titrant, and the points lie on two straight lines, in intersection of which establishes the equivalence point.

RESULTS AND DISCUSSION

The Effect of Ce(IV)

The polymerization yield is effected by Ce(IV) concentration up to a certain amount of Ce(IV) (5.10^{-3} M) in the case of the Ma–Ce(IV) redox pair. (See Figure 1). Above this value, Ce(IV) concentration does not affect the polymerization. Since substantial polymerization product could not obtain with this amount of Ce(IV) concentration in the case of AA, PA, SA, and AzA, 1×10^{-2} M Ce(IV) was used (Table I).

In the presence of oxalic acid, 54% yield is obtained using a lower Ce(IV) concentration (5.10^{-4} M), with monomer and HNO_3 concentrations held constant at 0.77 M and 0.065 M, respectively. Under these conditions, no polymerization occurs in the case of malonic acid. Differences in the yield might be due to the differences in orginates from the number of methyl groups of carboxylic acids used for initiation of acrylamide and reactivity of Ce(IV)-dicarboxylic acid.

The Effect of Chemical Structure of Diacids

In order to show the effect of the chemical structure of dicarboxylic acid on the polymerization yield, different concentration of those acids were used in the absence of HNO_3 (Table I). Monomer and Ce(IV) concentrations were held constant at 0.77 M and 1×10^{-2} M, respectively.

The possibility of intermolecular cyclization of dicarboxylic acids during electrochemical polymerization is known[21]. As can be seen from Table I, the higher the yield, the lower the molecular weight (molecular weight calculated from the intrinsic viscosity measurement M_v and number-average molecular weights M_n) of the polymer in the case of

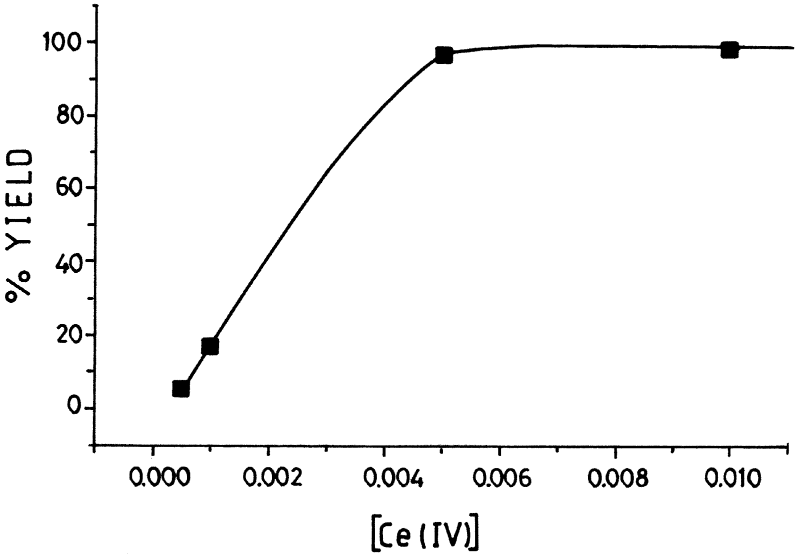

FIGURE 1 The effect of Ce(IV) concentration on the polymerization yield in the presence of malonic acid. $[HNO_3] = 0.065\,M$, $[AAm] = 0.77\,M$, [Malonic acid] $= 10^{-2}$, temperature = 30°C, time = 60 min.

pimelic acid, which has 5 methylene groups, probably due to the more termination with Ce(IV).

PAAm prefers the cyclization in this condition rather than allow to continue to grow the chain. Conformation of the molecule brings the two carboxylate groups near one another and cyclization of molecule might be occurred by termination with Ce(IV), which Ce(III) may partly belong to this cyclic PAAm. This cyclization capacity in the polymer chain in the case of Ce(IV)-pimelic acid redox pair, can explain the lower molecular weight of PAAm in Table I.

Molecular Weight Determination by Conductometric Analysis

A comparison of molecular weight determined by conductometric titration results and the viscometric method is given in Table I. The M_n values were calculated from conductometric analysis by (2):[24]

$$M_n = n \cdot 10^6/\mathrm{m} \qquad (2)$$

where n is the number of groups which can be determined per macromolecule and m is the end group concentration in microequivalents per gram. The conductometric titration curves of polymers, in the case of the Ce(IV)-dicarboxylic acid redox system, are given in Figure 2. The number average molecular weights were calculated from the equivalence of these curves as described in a previous paper[25].

The molecular weight (M_n) of resulting polymers were found to depend on the dicarboxylic acid concentration used. Doubling the acid concentration gives a product with about twice the molecular weight. The yield of polymerization was high and M_n values were in good agreement with the M_v values, if proper concentration of dicarboxylic acid was used for each acid type. The effect of the number of the methylene groups on the yield of polymers is shown in Figure 3. As it can be seen, if we leave out the OA ($n=0$) in these series, there is a zigzag relationship between the yield and n value in the acids while molecular weight results do not show this kind of relationship (Table I). Except AzA, the yield of the even n numbers of the acids were lower than those of the odd numbered ones. The lowest yield (1.00%) in the case of AzA in these series by using the same amount of dicarboxylic acid, might be due to the limited solubility of AzA at this concentration (8×10^{-3} M). Since the polymerization of AAm is initiated by the radicals (MA, AA, PA, SA, AzA) obtained by the reaction of corresponding acids with CAN, the low solubility of AzA in these series (1.4, 2.52, 0.16, and 0.10 gr/100 ml. for AA, PA, SA, and

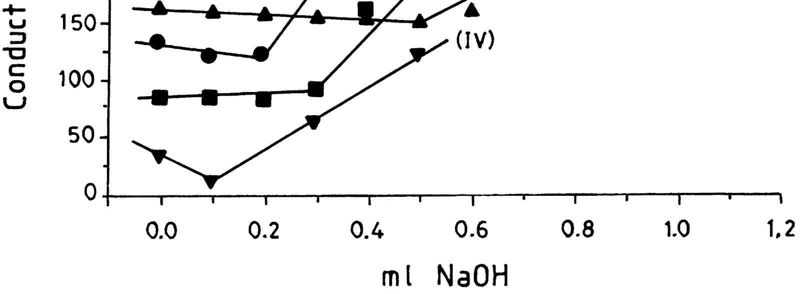

FIGURE 2 Conductometric titration curves for malonic (I), adipic (II), pimelic (III), suberic (IV), and azealinic (V) acids and Ce(IV) initiated PAAm with NaOH.

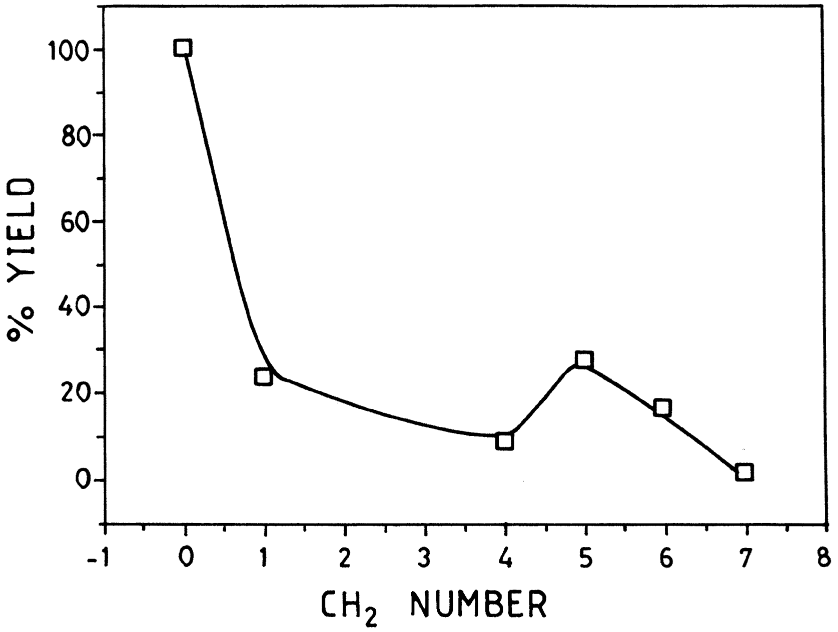

FIGURE 3 The effect of CH_2 number on the yield and molecular weight of polymers.

AzA, respectively) also lowers the chain length of the resulting PAAm ($M_v = 6000$, $M_n = 10000$).

FT-IR Results

The FT-IR spectra of polymers obtained by Ce(IV)-oxalic acid(I), malonic acid (II), adipic acid (III), pimelic acid (IV), suberic acid (V), and azealinic acid (VI) redox systems are shown in Figure 4. The spectra show characteristic peaks of both carboxylic acid and polyacrylamide. The strong and broad peaks due to C=O, aliphatic C–H and NH_2 stretching are seen at around 1650, 290, and 3400 cm^{-1}, respectively. It is known[21] that is the electrolysis of carboxylic acids ester formation is possible. In our case the peaks at approximately 1100 cm^{-1} may be correspond to possible ester structures in the polymerization mixture. The sharp peak at 1200 cm^{-1} corresponding to –CH bending in the polymer chain in the PAAm sample initiated with pimelic acid-Ce(IV) redox pair, where the

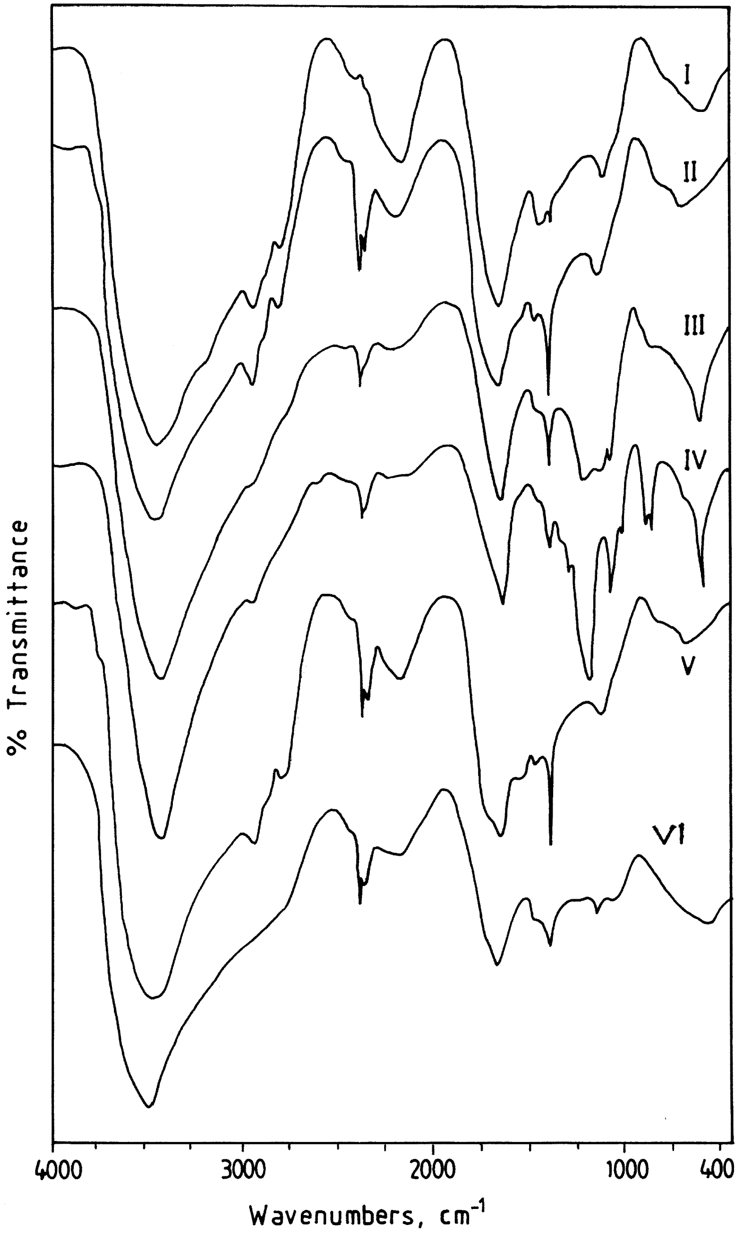

FIGURE 4 FT-IR spectra of Ce(IV)-oxalic (I), malonic (II), adipic (III), pimelic (IV), suberic (V), and azealinic (VI) acids.

acid has 5 CH_2 groups between the two carboxyl groups might be due to the cyclic conformation as explained above.

Theoretical Calculations

The zigzag correlation between the melting point and the *n* value in the acids is well known. In order to gain further information about the relation of some other properties of acids and the *n* values, the formation enthalpies of carboxylic acids were obtained by semiempirical quantum mechanical calculations using the MOPAC program with AM 1 Hamiltonian. The enthalpies were found high for carboxylic acids which have 4 and 6 methyl groups between the carboxyl groups and low for the acids which have 5 and 7 methyl groups (Table II).

The results are also consistent with the results reported by Muraishi et al[22]. E_a values of the even *n* members of the dicarboxylic acid series except for malonic acid, where higher than those of the odd-membered ones. It can be assumed that this property depends on whether an acid contains an even or odd number of carbon atoms because of the zigzag structures in dicarboxylic acid[26]. The zigzag correlation was also found by Takasuka et al.[23] between the percentage of the double cyclic intermolecular hydrogen-bonded molecules and the *n* value of the acids.

It is known that when a carboxylic acid reducing agent is used, the same functional group may be present as an end of the polymer chain. The zigzag relation between the different properties of acids and the *n* numbers might be explained by the similar zigzag correlation between the polymerization yield and *n* numbers in the same acids (Figure 3).

CONCLUSION

Some important conclusions have been reached by discussing the *n* values of acids and the reactant concentrations with the resulting

TABLE II The Relation between the Melting Point, the Formation Enthalpy and Type of Acid

Carboxylic acid	MP, (°C)	ΔH_f (k·cal·mol^{-1})
AA ($n = 4$)	152–154	11.72
PA ($n = 5$)	103–105	1.00
SA ($n = 6$)	139–142	11.80
AzA ($n = 7$)	109–111	1.00

n = number of methylene groups.

molecular weight of polymers. In summary we would like to state that the molecular weight and yield of Ce(IV)-dicarboxylic acid initiated polyacrylamides are driven by the number of methyl groups between the two carboxyl groups in these acids used. Consequently, if the Ce(IV)/dicarboxylic acid ratio is suitably selected for each acid, low or high molecular weighted PAAm could be synthesized.

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