Temperature Dependence of the Reaction between Some Metal Oxides and Polyacrylic Acid

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Synopsis

The temperature dependence of the reaction between some metal oxides and an aqueous solution of polyacrylic acid was investigated using the infrared measurements. The obtained data indicated that the divalent metal oxides MgO, ZnO, and PbO react rapidly with the polyacrylic acid forming carboxylate salts. The bonding between the acid groups and these metals is purely ionic in character. The reactivity between these metals and the carboxylic acid is inversely proportional to the radius of metal ions. The reaction of Bi_2O_3, Cr_2O_3, and TL_2O_3 is far from complete. However, SiO_2 reacts slowly with polyacrylic acid at 0°C only. The results provided strong evidences that the rate of reaction between some metal oxides and polyacrylic acid depends on the temperature of reaction, This rate of reaction is enhanced as the temperature is lowered.

INTRODUCTION

In the past few years infrared spectroscopy has been the most important tool for the characterization of the chemical and physical nature of dental zinc polyacrylate cements.[1-7] Crisp et al.,[1] for example, studied the reaction between metal oxides and the aqueous solutions of polyacrylic acid by following the changes in their infrared spectral features. They concluded that oxides of divalent metals form cement gels more readily than oxides trivalent metals. The Mg, Ca, and Zn polyacrylate gels are purely ionic and are therefore bound to the chains by electrostatic interaction.

Until the present time the temperature dependence of the reaction between the metal oxides and polyacrylic acid has not yet been fully investigated. The aim of the present study is to investigate the temperature dependence of the reaction between metal oxides and polyacrylic acid. The effect of heating on the properties of the cement after setting is also investigated. The study will be carried out using infrared absorption spectroscopy.

EXPERIMENTAL

The commercial polycarboxylate cement used in the present study was Lumicon (Bayer). The liquid is an aqueous solution of polyacrylic acid 45% (w/w) and the powder is zinc oxide 90% and MgO 10% (w/w).

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Different spec pure metal oxides such as MgO, ZnO, Bi_2O_3, GeO, SiO_2, CuO, Cr_2O_3, PbO, Tl_2O_3, NiO, SnO_2, and Al_2O_3 were mixed with polyacrylic acid at a ratio 1 : 1.

In this study, polyacrylic acid was thoroughly mixed with the metal oxide on a glass slide which was kept at the required temperature (such as 0, 25, 50, and 90°C) for 30 min. The infrared measurements were carried after 24 h from the setting.

The infrared measurements were carried out on Beckman Spectrophotometer 4250 using KBr disc technique.

RESULTS AND DISCUSSION

In the present study the reaction between each of the metal oxides MgO, ZnO, PbO, Bi_2O_3, Ti_2O_3, SiO_2, Cr_2O_3, NiO, CuO, Fe_2O_3, Al_2O_3, and SnO_2 and an aqueous solution of PAA was investigated by following the changes in their spectral features. The effect of temperature on the rate of reaction was also studied.

Figure 1 illustrates the infrared spectra of the compound resulted from the reaction between MgO and the aqueous solution of PAA at different temperatures, namely 0, 25, 50, and 90°C for 30 min. The spectra of the samples show

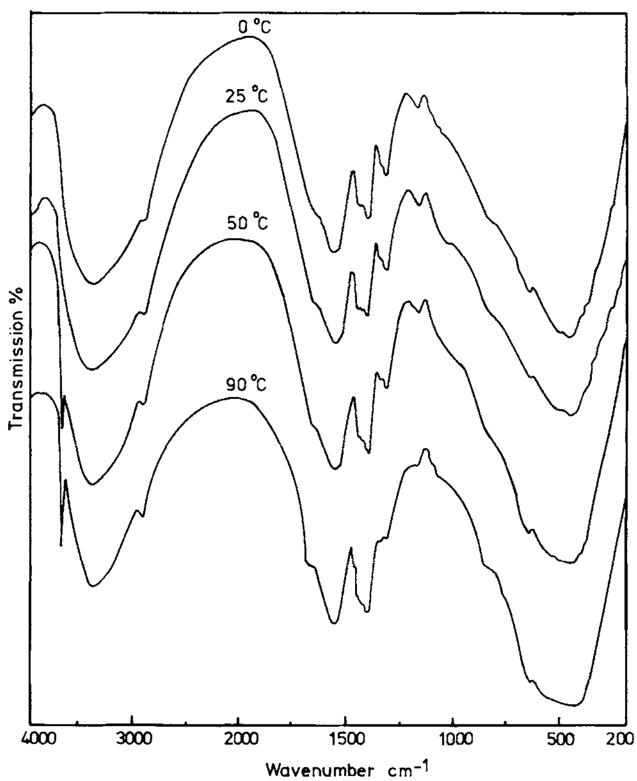

Fig. 1. IR spectra of polyacrylate cement containing MgO at different temperatures.

strong absorption at the frequency 1565 cm^{-1} and medium absorption at 1400 cm^{-1} which are due to asymmetric and symmetric stretching vibrations of the COO^- structure, respectively. It is easy to notice from Fig. 1 that the spectrum of Mg-polycaroxylate prepared at 25°C shows a very weak shoulder at 1725 cm^{-1}, whose intensity slightly increases with raising the temperature to 50 and 90°C and decreases with lowering the temperature to 0°C.

Figure 2 indicates that the reaction of ZnO with polyacrylic acid is rapid. The asymmetric carboxylate stretching band appears at 1575 cm^{-1} with a definite shoulder at 1725 cm^{-1}. The positions of the band and shoulder do not change with increasing the temperature from 0°C up to 90°C, but the intensity of the shoulder at 1725 cm^{-1} appears more intense in the spectra of the samples heated at 00°C and 90%. As this band corresponds to residual acid, this means that part of the acid group does not take part in the reaction at 50°C and 90°C.

The reaction between PbO and PAA at different temperatures was also investigated. The IR spectra of the resultant compounds are shown in Figure 3. This figure indicates that this reaction is rapid. The spectra of the samples formed at 0°C and at room temperature (25°C) exhibit strong absorption band at 1545 cm^{-1} and a shoulder at 1725 cm^{-1} due to the residual acid groups. Raising the temperature to 50°C and 90°C causes an increase in the intensity of the 1725 cm^{-1} band and a remarkable decrease in the intensity of that at 1545 cm^{-1}. This result gives strong evidence that the rate of reaction depends on the temperature of reaction, it is enhanced as the temperature is lowered.

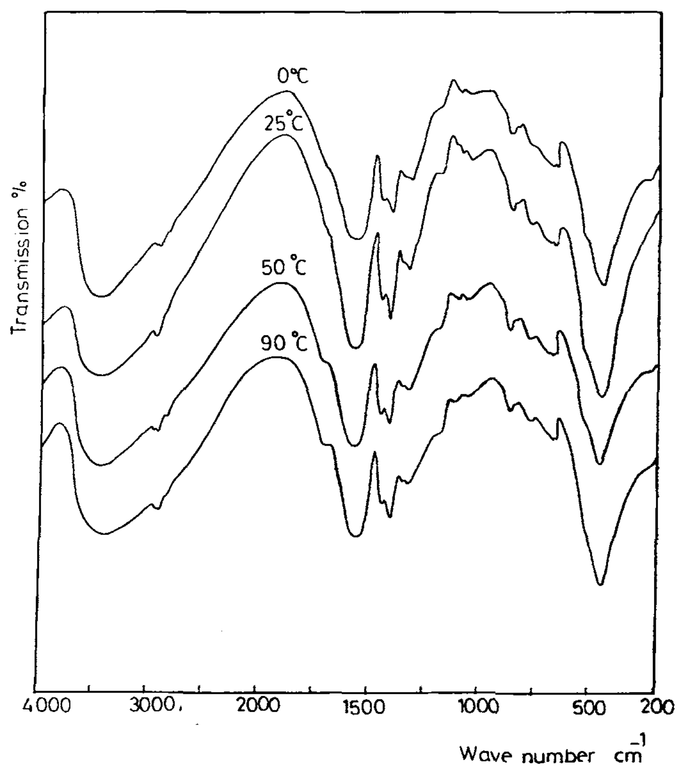

Fig. 2. IR spectra of polyacrylate cement containing ZnO at different temperatures.

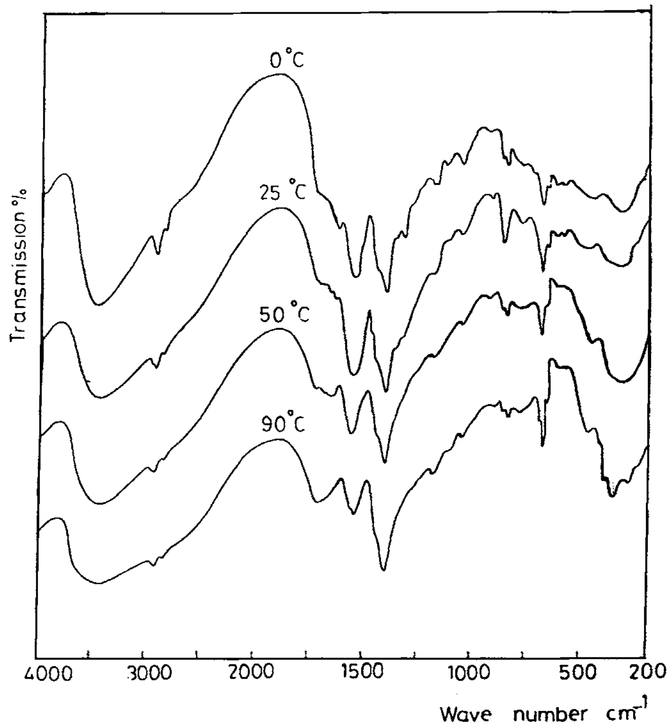

Fig. 3. IR spectra of polyacrylate cement containing PbO at different temperatures.

It is apparent from Figs. 1–3 that the weak shoulder—appearing in the spectrum of Mg-polycarboxylate at 1725 cm^{-1} due to the residual acid groups become more intense in the spectrum of Zn-polycarboxylate while it appeared as a definite band in the spectrum of Pb-polycarboxylate. It can also be noticed from these figures that the asymmetric COO^- band appears at the frequencies 1565, 1575, and 1545 cm^{-1} in the spectra of Mg, Zn-, and Pb-polycarboxylates, respectively.

The foregoing considerations can lead to the conclusion that the divalent metal oxides Mg, Zn, and Pb react rapidly with polyacrylic acid forming polycarboxylate salts. The bonding between the acid groups and these metals is purely ionic in character. Moreover, based on the changes of the intensity of the band corresponding to the residual acid group one can come to the conclusion that the reactivity of Mg, Zn, and Pb follows the trend Mg > Zn > Pb. This provides strong evidence that the reactivity of the mentioned metals is inversely proportional to the radius of the metal ions.

Figure 4 shows the spectrum of the compound obtained by mixing bismuth oxide (Bi_2O_3) and the aqueous solution of PAA. It is clear that it exhibits, in addition to the characteristic bands of the liquid, a weak band at 1550 cm^{-1} which can be attributed to COO^-, this provides strong evidence that bismuth oxide reacts slowly with the liquid.

Detailed studies of the spectra of Bi_2O_3—containing samples performed at various temperatures reveals that the temperature has no observable effect on the reaction between bismuth oxide and the aqueous solution of PAA.

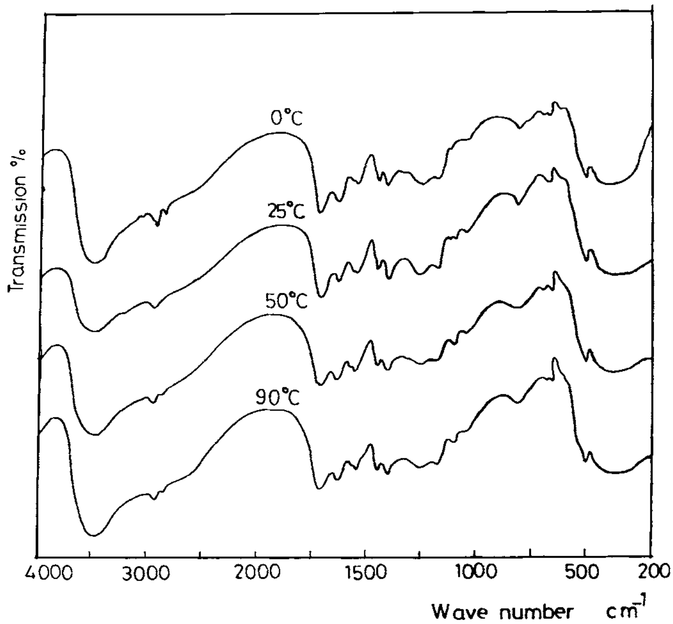

Fig. 4. IR. spectra of polyacrylate cement containing Bi_2O_3 at different temperatures.

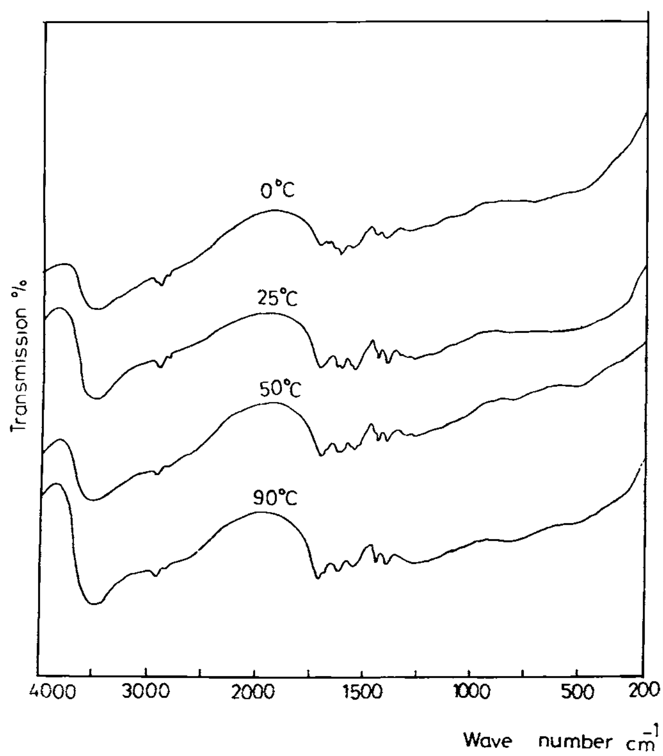

Fig. 5. IR spectra of polyacrylate cement containing Tl_2O_3 at different temperatures.

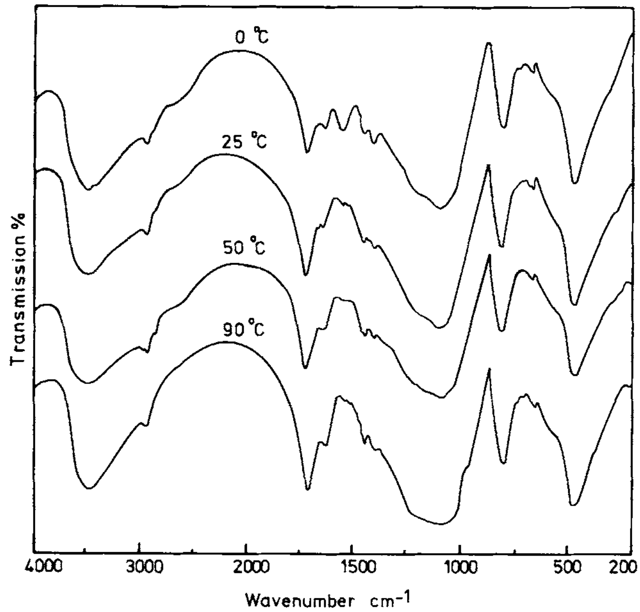

Fig. 6. IR spectra of polyacrylate cement containing SiO_2 at different temperatures.

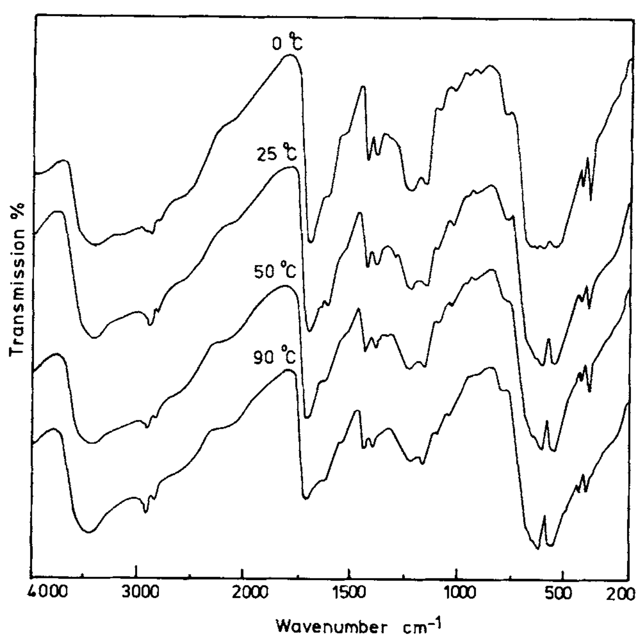

Fig. 7. IR spectra of polyacrylate cement containing Cr_2O_3 at different temperatures.

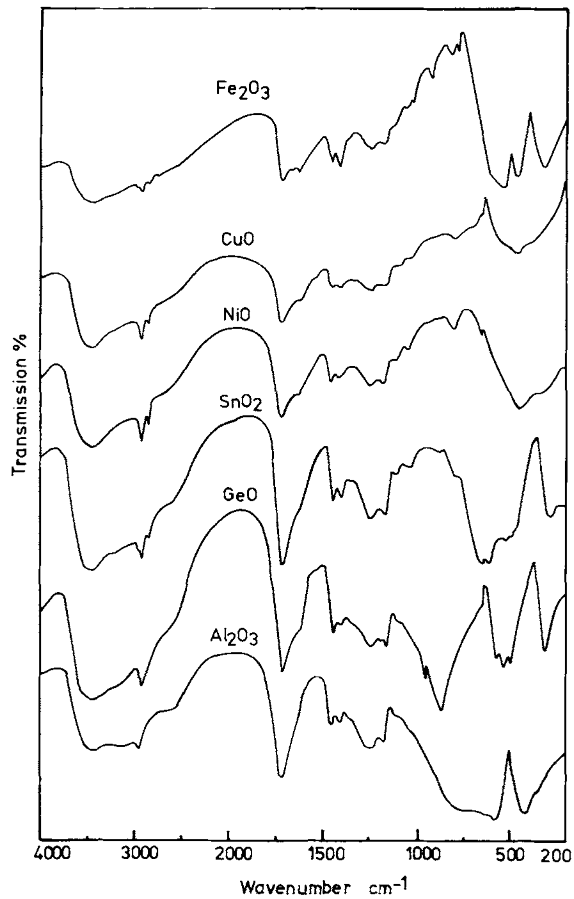

Fig. 8. IR spectra of polyacrylate acid with different metal oxide.

The spectra of the mixtures formed by adding thallic oxide (Tl_2O_3) with the aqueous solution of PAA show bands at the frequencies 1725, 1625, and 1550 cm^{-1}. The appearance of the 1550 cm^{-1} proves that a slow reaction takes place between the two materials. It appears from Figure 5 that as the temperature increases, the intensity of the 1725 cm^{-1} band due to the residual acid group increases while the intensity of the band at 1550 cm^{-1} decreases.

Silicon oxide was also thoroughly mixed with an aqueous solution of PAA at 0, 25, 50, and 90°C. The spectrum of the sample mixed at 0°C shows, in addition to the characteristic bands of the liquid and the silicon dioxide a weak band at 1550 cm^{-1} due to the ionized carboxylate group. This band disappears from the spectra of the mixtures formed at higher temperatures as shown in Figure 6. This result proves that the reaction between silicon oxide and the aqueous solution of PAA depends on the temperature of reaction. The result proves also that the reaction between SiO_2 and PAA occurs only at 0°C and it is very slow.

Figure 7 indicates that the resultant spectrum of the compound of Cr_2O_3 and the liquid obtained at 0°C exhibit a strong band at 1725 cm^{-1}, a broad shoulder

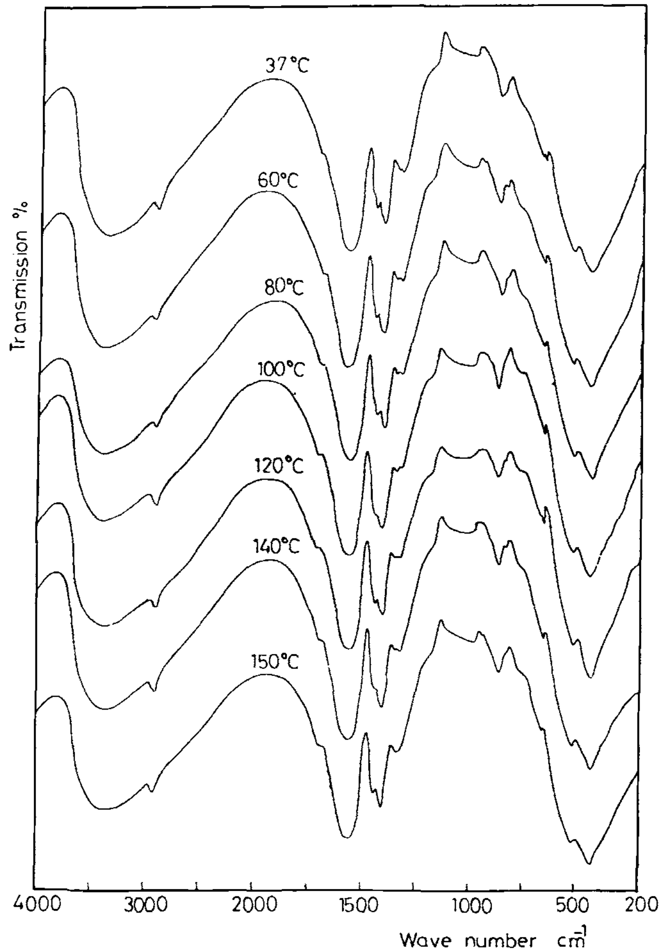

Fig. 9. Effect of mixing temperature on the IR spectra of commercial polycarboxylate cement.

at 1635 cm^{-1}, and a strong shoulder at 1550 cm^{-1} which indicates that at 0°C, Cr_2O_3 reacts very slowly with the liquid. The intensity of the shoulder at 1550 cm^{-1} decreases with increasing the temperature of reaction up to 90°C.

The reaction between the metal oxides NiO, CuO, GeO, Fe_2O_3, Al_2O_3, and SnO_2 and the aqueous solution of PAA at the temperatures 0, 25, 50, and 90°C for 30 min has also been studied. Careful analysis of the infrared spectra of the resulted mixtures revealed that at any given temperature, these metals do not react with PAA, since the resultant spectra show no evidence of new bands or any changes in the diagnostic bands of each of the two components in the mixture as shown in Figure 8.

The commercial zin poly carboxylate cement formed at room temperature was then heat treated at different temperatures from 25°C to 180°C. The I.R. spectra of the heat treated samples are shown in Figure 9. The absorbances (A) of the bands at 1575 and 2950 cm^{-1} were measured by using the baseline method. The values of (A 1575 cm^{-1}/A 2950 cm^{-1}) were recorded and are given in Table I.

TABLE I
The Ratio between A 1575 cm^{-1}/A 2950 cm^{-1} for Polycarboxylate Cement at Different Temperatures after the Reaction

Temperature (°C)	A 1575 cm^{-1}/A 2950 cm^{-1}
Room temp.	1.316
37	1.333
50	1.358
60	1.335
70	1.343
80	1.355
90	1.358
100	1.341
120	1.388
140	1.452
150	1.473

It is apparent from Table I that the ratio (A 1575 cm^{-1}/A 2950 cm^{-1}) assumes more or less constant value over all temperatures up to 120°C. Above 120°C, this ratio shows slight increases as the temperature increases.

The glass transition of PAA is about 127°C and this temperature is affected by the presence of ZnO,[8] and the change in this ratio after 120°C may be attributed to the glass transition.

Based on the above mentioned consideration one can conclude that the reaction between the metal oxides MgO, ZnO, and PbO takes place more rapidly with polyacrylic acid to form a carboxylate salt. It was found that the bonding between acid groups and these metal oxides are purely ionic in character. The reactivity of these metals follows the trend Mg > Zn > Pb, which means that the reactivity is inversely proportional to the radius of the metal ions. The reaction of Bi_2O_3, Cr_2O_3, and Tl_2O_3 is however far from complete. On the other hand, SiO_2 reacts slowly with PAA at only zero temperature. The oxides Al_2O_3, SnO_2, Fe_2O_3, CuO, GeO, and NiO are unreactive. This means that the reactivity between the carboxylic acid polymer and the metals is sterrically affected by the ionic radius of the metals. The sterric rendrence arrised by the increase of polycarboxylate ions entered in the reaction. The results provided strong evidence that the rate of reaction of the oxides ZnO, PbO, Tl_2O_3, Cr_2O_3, and SiO_2 depends on the temperature of reaction, it is enhanced as the temperature is lowered.

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