

PEP, conformational stabilities, IR and VCD analysis of the Co(en)_3^{3+} , $\text{Co(en)}_3\text{Cl}_2$ and $\text{Co(en)}_3\text{Cl}_3$

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Abstract

Conformational stabilities of the transition metal complexes of the Co(en)_3^{3+} , $\text{Co(en)}_3\text{Cl}_2$ and $\text{Co(en)}_3\text{Cl}_3$ are studied using Density Functional Theory (DFT/B3LYP/6-31**). The deformation potential energy profiles (PEPS), pathways between different isomeric conformations, were determined using the computer program Gaussian 03. Relative conformational energies of the O(ZZZ), O(ZZ6), O(Z66) and O(666) of the Co(en)_3^{3+} are 1.14, 0.46, 0.17, and 0.0 kcal/mol respectively. These numbers are small compared to the barrier heights for reversible phase transitions: 44.8, 44.2, and 43.6 kcal/mol respectively. The IR and VCD calculations were carried out for all of the conformations between 0 – 3500 cm^{-1} and are presented as VCD and IR absorption spectra.

Introduction

Transition metal complexes of the general form M(en)_3^{n+} , because of being ideal host lattices for single crystals, are the subject of many studies, ¹⁻⁵. The complexes can take two enantiomeric conformations and can exist in four conformational isomers: with the C – C bond nearly parallel (6 – form) or oblique (Z – form) to the C_3 symmetry axis in the K – conformation and denoted by K(666), K(66Z), K(6ZZ) and K(ZZZ). Degenerate with other enantiomers O(ZZZ), O(ZZ6), O(Z66) and O(666) respectively, the optimized structures of the Co complexes are presented in Fig. 1.

the highest for the net system due to better solubility of the curing agent and the reasonable mobility of the resin matrix.

Table 1: Dynamic DSC data for DGEBA/NDA/BaCO₃ composites at heating speed of 10 °C/min.



	OH _t	OH(J/gr-epoxy)	Peak cure onset	Peak maximum
No filler	-281.4	-	84	181.8
2phr filler	-249	-254.3	85	182.4
5phr filler	-224	-246.5	86	184
10phr filler	-221	-243.9	87	187
15phr filler	-158.2	-182	89	191.2

The highest cure onset temperature was also observed for the composite having 15 phr filler. This could be described through low reactivity of the curing agent in the epoxy matrix at this high level of loading. Figure 1 exhibits DSC curve of the cured composites. We used a model proposed by Chern and poehlein which is a semiempirical relationship based on free volume considerations to explain the diffusion control in the studied cure reaction.

Figure 1: DSC curves of DGEBA/NDA/BaCO₃ composites

When the degree of cure reaches a certain critical value a_c , diffusion control takes over and the diffusion-controlled rate constant K_d is given by:

$$K_d = K_c \exp [-C (a - a_c)] \quad (1)$$

Where, K_c is the rate constant for non-diffusion controlled kinetics and C is a constant. According to Rabinowitch method, the overall effective rate constant K_e could



be defined as:

$$1/K_e = 1/K_d + 1/K_c \quad (2)$$

Through combining Eqs. (1) and (2), a diffusion factor $f(a)$ in the following form has been defined and used to fit the experimental data.

$$f(a) = K_d = 1/1 + \exp[C(a - a_c)] \quad (3)$$

Where, C and a_c (the critical conversion) are two empirical parameters.

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