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ScienceDirect
European Polymer Journal 44 (2008) 1191–1199
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

Cole–Cole plot analysis of dielectric behavior of monoalkyl ethers of polyethylene glycol (C_nE_m)

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Received 5 June 2007; received in revised form 7 November 2007; accepted 13 January 2008
Available online 18 January 2008

Abstract

The complex permittivity of monoalkyl ether of polyethylene glycol (C_nE_m) was measured at 336.5 K at frequencies from 0.2 to 20 GHz. The number of bonded ethylene glycol units was varied from 1 to 120 to observe the effect of the PEG-chain length on the dielectric permittivity of the whole polymer. The measured real and imaginary parts of complex permittivity of these polymers were studied by the graphical analysis of the Cole–Cole plot as proposed by Havriliak and Negami. This analysis makes us understand that, in the high-frequency region above 9.7 GHz, the Cole–Cole plot of all C_nE_m is located on one single line. This phenomenon implies the same relaxation mechanism of all C_nE_m in this frequency region. It is found that the same relaxation mechanism of the dipoles of the hydroxyl group in *n*-alcohol contributes to the dipole relaxation of C_nE_m. In the low-frequency region, the arc of the Cole–Cole plot has the same shape as pure PEG, but it is scaled-down linearly following the decrease of the number of PEG units bonded to the *n*-alkanes. This phenomenon explains the linear contribution of ether dipoles, existing in bonded PEGs, on the complex permittivity of C_nE_m in the low-frequency region.

Keywords: Complex permittivity; Ether dipoles; Hydroxyl dipoles; Dielectric constants; Polymers; Havriliak–Negami's graphical analysis

1. Introduction

Dipolar losses in the microwave range are used in modern technology to accelerate thermal processing of polymers (tempering, curing etc.) [1–5]. Optimal heating conditions can be achieved by combining conventional and dielectric heating. A fast volumetric heating can affect the thermal decomposition kinetic of the polymers and, for example, prevent undesired oxidation reactions and decompositions. Furthermore, the presence of the electro-magnetic

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doi:10.1016/j.eurpolymj.2008.01.016

field has been shown to lower the onset temperature of chemical reactions and also can lead to different reaction products.

In molecular systems submitted to microwave radiation the conversion of electro-magnetic energy into heat is essentially due to the interaction of the electric field with electric dipoles. Apolar molecules such as *n*-alkanes or paraffins are not suitable for microwave heating. On the other hand, polar structures such as polyethylene glycols (PEG) are dissipative [6–8]. In this study, we investigated the dielectric properties of molecules with the general formula: $H(CH_2)_n$–$(OCH_2CH_2)_mOH$. These are called monoalkyl ethers of polyethylene glycol and are described shortly as 'C_nE_m' in this paper. These molecules are composed of one straight part containing electric dipoles chemically linked to an inert *n*-alkane part. We investigated how the PEG-chain length, *m*, effects the dielectric properties of the whole compounds. The number of chemically bonded PEG-chain was varied between 1 and 120. PEG3000 was also studied for comparison.

To analyze the measured dielectric functions, we plotted the real part of the complex permittivity in the *x*-axis and the imaginary part of that in the *y*-axis. This is known as the Cole–Cole plot. In this paper, we use Havriliak and Negami's analytical method [9,10], which succeeded to explain the skewed and arcuated shape of the Cole–Cole plot of polymers. The definitions and theoretical background of this analytical method are briefly summarized in chapter 2. This analytical technique helps us to understand the effect of chemically bonded PEG to the *n*-alkane on the shape and size of the dielectric functions in the Cole–Cole plot. Previous studies about dielectric relaxation mechanisms of alcohols and ethylene glycols are introduced to analyze the effect of hydroxyl and ether dipoles on dielectric relaxation of C_nE_m.

2. Definitions and theoretical background of the Cole–Cole plot

The analysis of the measured complex permittivity is usually performed by a curve-fitting technique based on, typically, one of the following models: Debye model, Cole–Cole model, Davidson–Cole model, Havriliak–Negami model and KWW model. The curve-fitting analysis is typically used to find the relaxation time. In addition, the Cole–Cole plot of the dielectric constants has also been used to analyze the dielectric parameters. A graphical analysis using Cole–Cole plot proposed by Havriliak and Negami [9,10] is efficiently applied, especially in the case of polymers. In their work they studied the Cole–Cole plots of many polymers and found that all these plots have approximately the same shape. The curve becomes linear in the high-frequency region and is arcuated in the low-frequency region.

In order to represent this behavior quantitatively, they proposed the following relaxation function:

$$\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty}=\{1+(\mathrm{i}\omega\tau_0)^\alpha\}^{-\beta} \tag{1}$$

where ε^* is the complex permittivity, ε_∞ is the limited high-frequency dielectric permittivity, ε_0 is the limited low-frequency (static) dielectric permittivity, ω is the angular frequency and τ_0 is the average relaxation time. α is the distribution parameter indicating the broadness of the symmetric relaxation curve and β is the distribution parameter indicating the skew of the circular curve. Eq. (1) can be separated into the real and imaginary parts of complex permittivity $(\varepsilon', \varepsilon'')$ as follows [9]:

$$\varepsilon'(\omega)-\varepsilon_\infty=r^{-\beta/2}(\varepsilon_0-\varepsilon_\infty)\cos\beta\theta \tag{2}$$

$$\varepsilon''(\omega)=r^{-\beta/2}(\varepsilon_0-\varepsilon_\infty)\sin\beta\theta \tag{3}$$

where

$$r^2=\left[1+(\omega\tau_0)^{1-\alpha}\sin\alpha(\pi/2)\right]^2+\left[(\omega\tau_0)^{1-\alpha}\cos\alpha(\pi/2)\right]^2 \tag{4}$$

$$\theta=\arctan\left[\frac{(\omega\tau_0)^{1-\alpha}\cos\alpha(\pi/2)}{1+(\omega\tau_0)^{1-\alpha}\sin\alpha(\pi/2)}\right] \tag{5}$$

Eqs. (2)–(5) indicate that, with $\omega\tau_0$ going towards infinitive, $\varepsilon'(\omega)$ reaches ε_∞ and $\varepsilon''(\omega)$ reaches zero. In addition, with $\omega\tau_0$ going towards zero, $\varepsilon'(\omega)$ reaches ε_0 and $\varepsilon''(\omega)$ reaches 0. For these reasons, two of the dispersion parameters, ε_∞ and ε_0, can be evaluated as the high- and low-frequency intercepts of the experimental $\varepsilon'(\omega)$ with the real axis of Cole–Cole plot.

3. Experimental method

3.1. Materials

Monoalkyl ethers of polyethylene glycol (C_nE_m) were obtained from Zschimmer & Schwarz GmbH & Co. KG in Germany ($n = 18$ or $n = 22$, $1 \leqslant m \leqslant 120$). The number of PEG-chain length was varied between 1 and 120. The chemical struc-