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Dielectric Properties of Hyperbranched Polyesteramide with Long Alkyl Chain End Groups

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Summary: Hyperbranched polyesteramides were prepared using phethalic anhydride (Ph An) or maleic anhydride (M An) as an A_2 monomer and diethanol amine (DEA) as $B'B_2$ monomer. Bulk condensation technique was used to synthesize polymers with both OH and modified polymers with long alkyl chain end groups. The prepared polymers were characterized using ^{1}H-NMR, FTIR and TGA. Solution viscosity for hyperbranched polyester amide with hydroxyl end groups was measured as well. Dielectric and electric properties of the modified samples were investigated over a range of frequency and temperatures. No relaxation peak is noticed in the dielectric spectrum $\varepsilon(\nu)$ at various temperatures. The illustration of the imaginary part of the electric modulus M'' versus frequency shows a peak which is shifted towards higher frequency in increasing temperature.

Keywords: dielectric loss; electric modulus; hyperbranched polymers; modification; permittivity

Introduction

Over the last two decades, hyperbranched polymers have received much attention due to their unique chemical and physical properties as well as their potential applications in coatings, additives, drug and gene delivery, macromolecular building blocks, nanotechnology and supramolecular science. Hyperbranched polymers can be prepared by means of 1) single monomer methodology (SMM) through the polymerization of an AB_2 or latent AB_n monomer. 2) double monomer methodology DMM. SMM consists of at least four components: a) polycondensation of AB_n monomers,[1] b) self-condensing vinyl polymerization,[2] c) self-condensing ring-opening polymerization,[3] d) proton transfer polymerization.[4] In DMM, direct polymerization of two suitable monomers or a monomer pair give rise to hyperbranched polymer. A classical example of DMM, the polymerization of A_2 and B_n $(n > 2)$ monomers is well known. Recently, a novel DMM the in situ formation of AB_2 intermediates from specific monomer pairs has been developed.[5,6] Many commercially available chemicals can be used as the monomers in these systems which should extend the availability and accessibility of hyperbranched polymers with various new end groups, architectures and properties. Hyperbranched polymers prepared from direct polymerization of A_2 and $B'B_2$ are reported.[7–12] The monomer $B'B_2$ contains one B' functional group and two B_2 functional groups which all can react with the A group. But the reactivates of B' and B groups are different from each other. The difference in reactivity can be attributed to the difference in chemical environment or the chemical structures of the two functional groups. An in situ AB_2 is formed from the reaction of an A of A_2 and a B group of $B'B_2$ during the initial period of the reaction. There is no border line between the generation of the intermediate and its polymerization. Also the propagation reaction generally occurs as soon as the intermediate is formed, it hardly can be separated. Hyperbranched

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polymers are characterized by their large number of end groups. Through modification of these end groups tailored properties are attainable for specific applications. In hyperbranched polymers the accessibility of the functional groups is quite good for small reagents. However, conversion decreases for polymers of high molecular weight and for large reagent molecules. Introducing new functional groups influence not only solubility and thermal behavior of the polymer, but they affect polarity and, in some cases, the dimension and the shape of the hyperbranched polymer in solution.[13] While most available literature has focused only on synthetic routes, dielectric relaxation is a powerful tool to study and characterize the dynamic behavior of these polymers. This method provides information about the molecular motions related to fluctuations of dipole moments. Several investigations of glass transition temperatures (T_g) in hyperbranched structures have correlated T_g's to the number of chain ends,[14] molecular weight[15,16] and recently the thickness of sample thin film (confinement effect[17–20]). The aim of the present work is to report the dielectric as well as electrical properties of such prepared and characterized samples when modified.

Experimental Part

Materials

Phethalic anhydride and maleic anhydrides were obtained from Labratory Rasayan, s.d.fine-chem Ltd. Stearic acid and methanol products of ADWIC, El Nasr pharmaceutical chemicals. Tetrahydrofuran (THF) was obtained from Labratory Rasayan.

Instruments

The samples were analyzed by ^{1}H NMR measured using JEOL ECA500 spectrometer operating at 500 MHz. DMSO-d_6 was used as solvent and internal standard. The spectra were measured at 303 K using 5 mm o.d. sample tubes.

FTIR spectra were recorded on Nexus 670, Nicolet, USA spectrometer using frequency range 4000–400 cm^{-1} with resolution 4 cm^{-1}. KBr pellet technique was used for measurements.

Thermogravimetric Analysis (TGA) was carried out in nitrogen atmosphere at a heating rate of 10 °C using the computerized Perkin Elmer (US, Norwalk, CT) TGA 7 – Unix system series.

A viscosity measuring unit AVS 350 was used to determine the relative viscosity (η_{rel}) of the unmodified polymers in *N*, *N* dimethylacitamide at 30 °C at a fixed concentration of 0.4 g dl^{-1}. In this case the liquid meniscus is sensed optoelectronically at the measuring levels. These precision devices always ensure the high accuracy of the capillary viscometer measuring principle even.

The dielectric measurements were carried out in parallel plate geometry. The samples were pressed at a temperature 20 to 30 °C higher than T_g. Fused silica ring with thickness of 125 μm was used as spacer material. Dielectric properties were measured in a frequency range 42 Hz to 5 MHz using computerized Hioki 3531 Z HiTESTER impedence meter. The temperature of the sample was varied by a temperature controlled system.

Synthesis of Aromatic Hyperbranched Polyester Amide Ar (PEA–OH)

7.4 g phethalic anhydride (0.05 moles) was charged in 3 neck flask, evacuated and filled with N_2. 7.88 g diethanol amine (0.075 moles) was added and the temperature was raised up to 140 °C. After complete dissolution of anhydride, the vacuum was applied again to remove H_2O. Aliquots of the reactants were taken to determine acid concentration by dissolving the sample in THF and titration against 0.1 N KOH in methanol. The reaction was stopped when the required molar mass was reached, yellowish viscous resin was formed. The polymer was poured while it is hot and glassy orange polymer was obtained (yield = 95%, Mn calculaed = 2000 g/mol, $\eta_{rel} = 1.209$). The prepared polymer showed good solubility in polar solvents.

^{1}HNMR (DMSO-d_6) δ ppm: 8.17–7.15 (aromatic ring, disubstituted), 5.58 (OH), 4.48 (CH_2–OCO, l), 4.22 (CH_2–OCO, d), 3.67 (CH_2 OH), 3.44–2.99 (N CH_2 t, l).

FTIR spectra: 3340 cm^{-1} (OH bonded), 2940 cm^{-1} (ν_{as}, CH_2) and 2840 cm^{-1} (ν_s, CH_2).1712 cm^{-1} N–C=O (amide I), 1606 cm^{-1}C=O ester linkage.

Synthesis of Aliphatic Hyperbranched Polyester Amide Al (PEA–OH)

16.96 g maleic anhydride (0.17 moles) was charged in 3 neck flask, evacuated and filled with N_2. 23.63 g diethanol amine (0.225 moles) was added and the temperature was raised up to 140 °C. After complete dissolution of anhydride, the vacuum was applied again to remove H_2O. Aliquots of the reactants were taken to determine acid concentration by dissolving the sample in THF and titration against 0.1 N KOH in methanol. The reaction was stopped when the reaction mixture turned yellowish viscous liquid. The polymer was poured while it is hot and glassy yellow polymer was obtained (yield = 95%, Mn calculated = 2000 g/mol, $\eta_{rel} = 1.206$).

(DMSO-d_6) δ ppm: 6.54–6.0 (alkene protons), 4.36 (OH), 4.17 (CH_2–OCO), 3.9 (CH_2–N), 3.73 (CH_2 OH), 3.52 (N CH_2 CH_2–OCO), 3.5 (N CH_2 CH_2–OH).

FTIR: 3405 cm^{-1} (OH bonded), 2937 cm^{-1} (ν_{as}, CH_2). 1732 cm^{-1} N–C=O (amide I), 1640 cm^{-1} (C=C) overlapped with 1634 cm^{-1}C=O ester linkage.

Example for Modification Reaction: Synthesis of Hyperbranched Polyester Amide Modified with Stearic Acid Ar (PEA-stearat)

A three neck flask was evacuated, filled with N_2 and loaded with 22.12 g phethalic anhydride and 18.9 g diethanol amine. The reaction started under stirring and the temperature was raised up to 140 °C. After complete dissolution of anhydride, vacuum was applied (5 mbar). After 3 hours 7.1 g stearic acid was added under N_2, then reduced pressure was applied again.

^{1}HNMR (DMSO-d_6) δ ppm: 8.17–7.15 (aromatic ring, disubstituted), 5.58 (OH), 4.48 (CH_2–OCO, l), 4.22 (CH_2–OCO, d), 3.67 (CH_2 OH), 3.44–2.99 (N CH_2 t, l), 2.2, 2.3 (esterified stearic acid) 2.18, 1.48, 1.23 and 0.85 (stearic acid alkyl chain).

FTIR spectra: 2917 cm^{-1} (ν_{as}, CH_2), 2849 cm^{-1} (ν_s, $(CH_2)_{16}$), 1464 cm^{-1} (δ_{as}, CH_3, δ_s $(CH_2)_{16}$), 1377 cm^{-1} (δ_s CH_3).

Results and Discussion

Hyperbranched polyester amide was prepared through bulk condensation of acid anhydride and diethanol amine which yielded high conversion and pure polymers. The method was described by Froeling[21] who and his group synthesized series of hyperbranched polyester amides using different acid anhydrides as A_2 monomers and diisopropanol amine as $B'B_2$. It is known that DEA is not the best candidate to be used as $B'B_2$ monomer since the presence of primary OH group leads to gelation through the undesired side product from the reaction of the OH group instead of the amine group. The remaining secondary amine in the formed ester would lead to discoloration and could react with the cyclic anhydride yielding an A_2B reactant that would rapidly lead to an undesired crosslinking. An important aspect of this work is to control the polymerization process to prevent gelation (i.e. cross-linking) of the copolymer. For the copolymerization process of this work, the ratio (r) of A-groups to B-groups (r = A/B), and/or the extent of reaction (p) are selected so as to avoid cross-linking. A hyperbranched polymerization system can be approximately modeled by assuming that $A_2 + B_3$ (a) A-groups only react with B-groups, and B-groups only react with A-groups, (b) cyclization reactions do not occur, (c) all A-groups exhibit equal reactivity regardless of the size and shape of the molecule to which they are attached, and (d) all B-groups exhibit equal reactivity regardless of the size and shape of the molecule to which they are attached. Using these assumptions, as an example, complete conversion of the minor component can be achieved for an $A_2 + B_3$ system without gelation when the ratio of A-groups to B-groups is less than 0.5 or greater than 2. As an alternative, gelation can be avoided by controlling the extent of conversion (completion) of the reaction. So, for a system in which the number of A and B groups are equal, gelation can be avoided if the reaction is terminated at or below about 70% conversion. In the case where either A-groups or B-groups are in excess (i.e., $r \neq 1$), the extent of reaction (p) is determined with respect to the minor reactant (the lesser of A and B), and r is the ratio of the minor to the major component. For real systems, using different molar ratios of either monomer works very well to avoid gelation. Ar (PEA–OH) was prepared using 1:1.5 molar ratio of phethalic anhydride to diethanol amine while for Al (PEA–OH) the used molar ratio was 1:1.3. Also, time factor is important since long reaction times lead to high probability of side reactions. In our work short reaction times were used (about 5 hours), of course lower molar masses are obtained as a result of reducing reaction time. But, in this way fully soluble polymers were synthesized and no gelation problem occurred. Glassy resins were obtained with good solubility in polar solvents such as methanol. DMF, N, N-DMAc and DMSO, only Al (PEA–OH) is soluble in water.

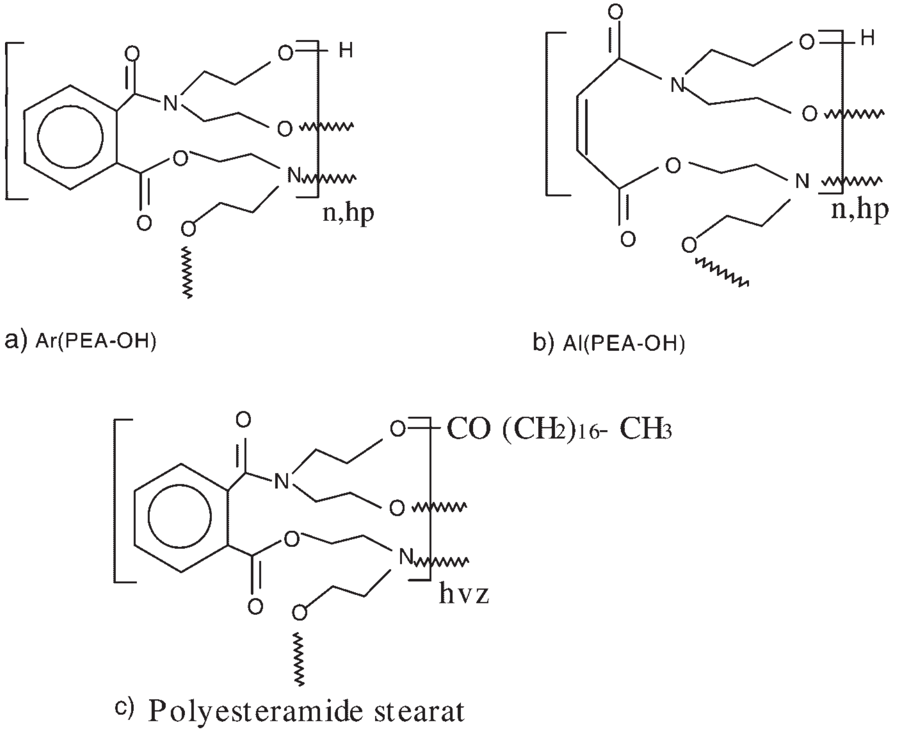
Depending on the molar ratio of the monocarboxylc acid to the other two components in the system, the monocarboxylic acid can be used as chain stopper or as end group modifier. When the amount of monocarboxylic acid is equal to $(n+3)$ which is the number of end groups, a polyester amide is obtained in which all end groups are modified. Normally, complete modification of hyperbranched polymers with long alkyl chain compounds is difficult due to the branches of the polymer. So, the long chain modifier groups are present on the periphery of the polyester amide, while the interior hyperbranched chains have hydroxyl end groups. The degree of modification was found to be 55% and the modified hyperbranched polymers were found to be soluble in DMSO/$CHCl_3$ and $CHCl_3$. Chemical structures of the prepared polymers are shown in Figure 1.

Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) was employed to study the thermal stability for the four different samples in the temperature range 50–500 °C. Figure 2 shows the thermogram for the PEA samples modified and unmodified. TGA showed that the modified aliphatic hyperbranched polymer has higher thermal stability in comparison with the other polymer samples which starts to degrade at 191 °C. It can be noticed that the aromatic hyperbranched polymer has the same thermal behavior either modified or not, the samples with stand temperature up to 115 °C. This may be attributed to the presence of aromatic ring which facilitates degradation. It can be noticed also from the degradation slope of Ar (PEA–OH) which is sharper than that for the aliphatic samples. Weight loss starts with complete degradation at 270 °C for all samples.

Dielectric Measurements

Figure 3 illustrates graphically the imaginary part ε'' of dielectric function ε^* as a function of frequency and temperature for the aliphatic- right, and aromatic, left hand side- modified polyester amide. Large values of ε'' at low frequency may reflect the high dc conductivity within the material and/or interfacial polarization between the sample and electrode. The systematic change in the spectrum is due to the modification treatment which reduces the density of the OH terminal groups in the polymer by about 55% as determined previously. This reduces hygroscopic character of the polymers since the long chain modifier groups ($C_{17}H_{35}$) are present on the periphery of the polyester amide, while the interior hyperbranched chains have hydroxyl end groups. It means clearly that the dielectric response here is mainly due to the long alkyl chains and not to the OH groups as in the case of unmodified polymers. The unmodified polymers, showed high tendency to adsorb water from the surrounding atmosphere, so, the dielectric parameters couldn't be measured without very serious precautions, which are not available in our lab. Even so, no remarkable relaxation



a) Ar(PEA-OH)

b) Al(PEA-OH)

c) Polyesteramide stearat

Figure 1.
Chemical structures for (a) aromatic PEA, (b) aliphatic PEA and (c) aromatic modified polyester amide.

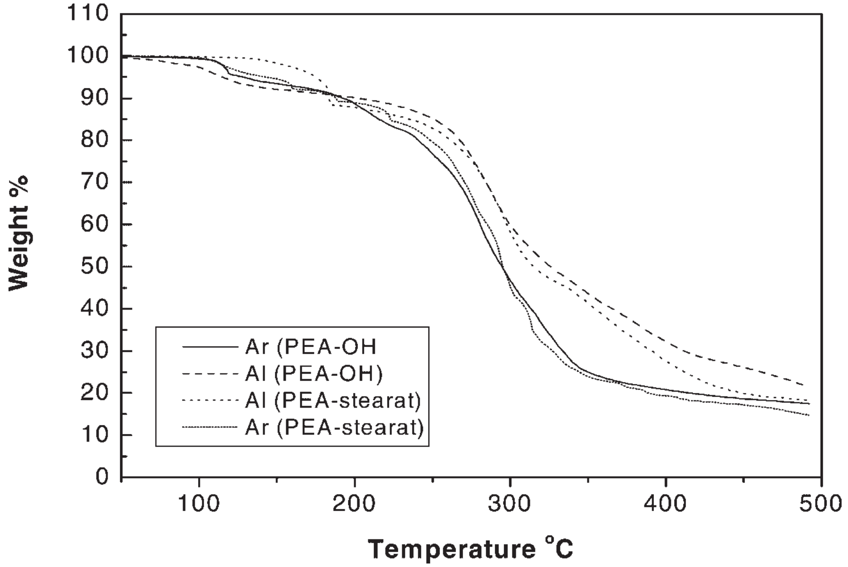


Figure 2.
TGA traces for unmodified and modified polyester amide.

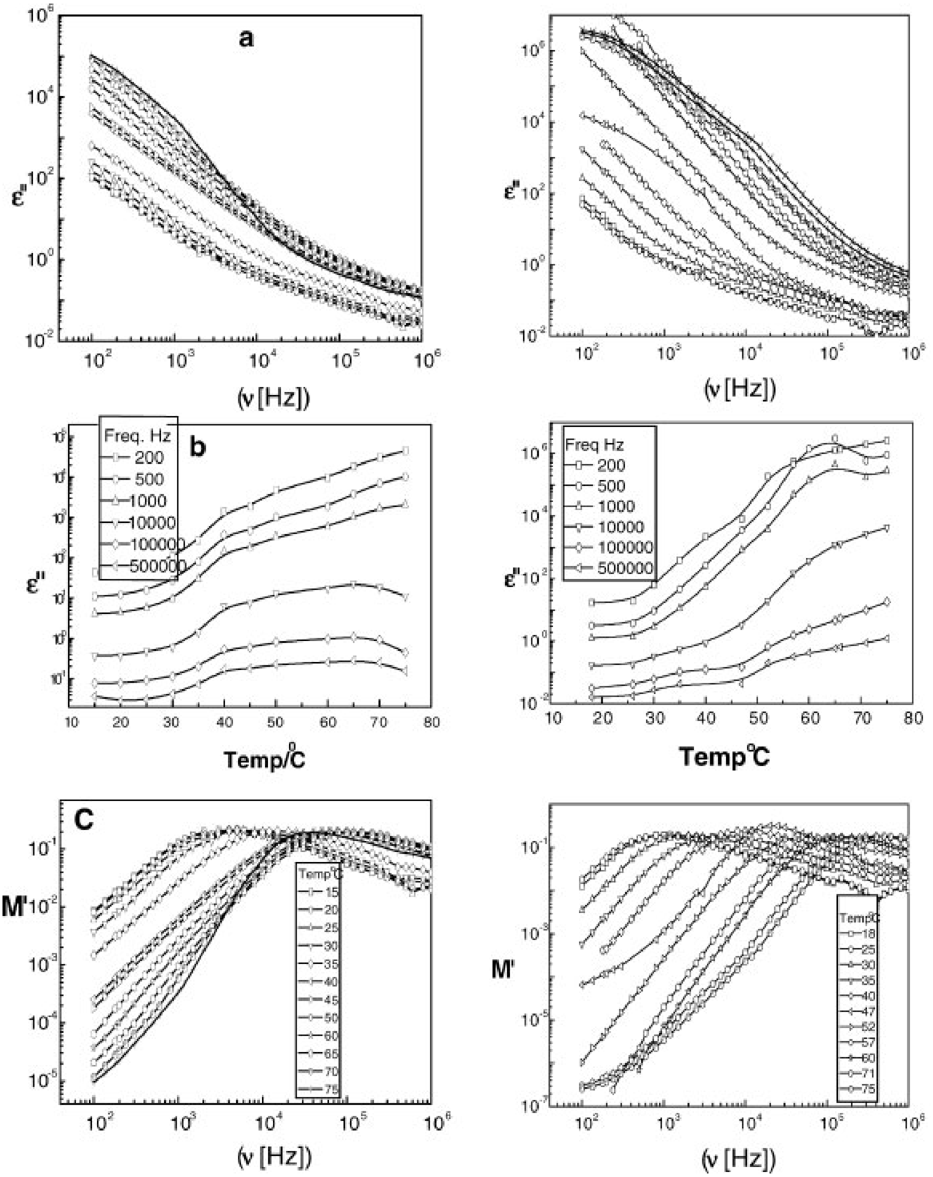


Figure 3.
Dielectric loss ε″as a function of frequency and temperature and the frequency dependence of the imaginary of the electric modulus M″ for the modified - aliphatic, right hand side and aromatic left hand side – polymers (the lines are guides for the eyes).

peak could be seen in the frequency and temperature ranges under consideration. For the aliphatic modified polyester amide, Al (PSA-stearat), the temperature dependence of the dielectric loss ε″ shows two trends like behavior. The melting range (30–40 °C) separates between both of them. Values of ε″ are higher in of liquefied polymers than those at lower temperatures solid polymers reflecting the increase of mobility. Further increase of temperature in liquid polymers did not affect the values of ε″ at higher frequencies. At lower frequencies, the increase of temperature increases the values of ε'' which may be attributed to the increase in dc conductivity. More inspection in Figure 3 leads to the clearly foundation of the liquid- solid families in Al (PSA-stearat), even in both cases, ε'' as a function of frequency has the same trend. The Ar (PSA-stearat) shows gradual effect of the temperature increasing on the ε'' reflecting the absence of the liquefaction process. At high temperatures and low frequencies, ionic conductance becomes significant. In low frequency dc conduction, the hopping of mobile charge carriers is rapid over low free energy barriers in alignment with the electric field, while they accumulate when high free energy barriers are encountered.[22,23] This results in a net polarization of the ionically charged system which contributes to permittivity ε' and dielectric loss ε''. At high frequencies, the periodic shift of the electric field prevents the accumulation of charges at high energy barrier sites, thereby eliminating the net polarization discussed above. Mathematically treated data in terms of electric modulus will prevent the contribution of dipole alignment from the conductive effects obscured it. The electric modulus $M^* = M' + iM''$ is defined as the inverse of the complex permittivity ε^*.

The imaginary part of the electric modulus M'' is illustrated graphically versus frequency at different temperatures as shown in Figure 3 (bottom) for both modified polymers. Only one broad peak is noticed here. The frequency of the maximum M'' is found to shift to the high value with increasing temperature. Such a shift

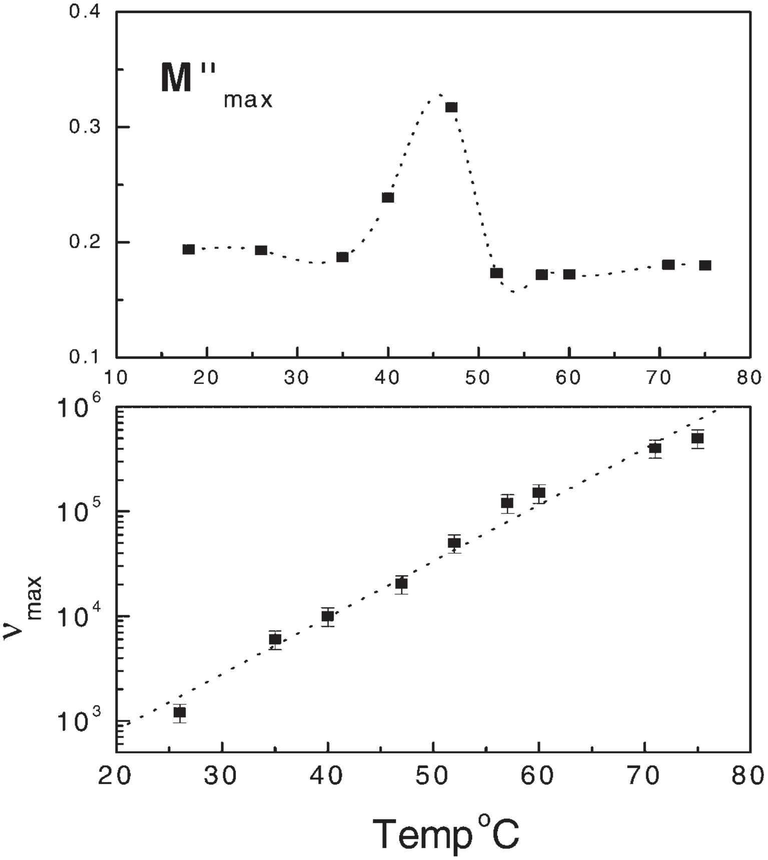


Figure 4.
The temperature dependence of M''_{max} values and relaxation rate for the Ar (PSA-stearat).

indicates an existence of a conductivity relaxation. There is also a gap of separation between the trends of liquid and solid with no effect of temperature on the maximum value of M″ in Al (PSA-stearat) whereas in case of Ar (PSA-stearat), a peak like behavior of M''_{max} as a function of temperature was found. The peak lies between 35 and 50 °C i.e. at the range of liquefaction process. On the other hand, the temperature dependence of the maximum peak position of M″ shows an Arrhenius relation. This may reflect that the process here is due to the terminal groups and not due to the glass transition process.

Conclusion

Polycondensation of phethalic anhydride or maleic anhydride as A_2 monomers and diethanol amine as $B'B_2$ monomer lead to hydroxyl functional hyperbranched polyester amides. Gelation was avoided through using higher concentration of $B'B_2$ monomer and short reaction times. Fully soluble resins were obtained which were characterized using NMR and FTIR. Partially stearic acid ester functionalized diethanol amide based hyperbranched polyester amides have been synthesized in a straightforward polycondensation reaction from calculated amounts of acid anhydride, diethanol amine and stearic acid. The modification of chain end groups was confirmed by NMR and FTIR. The dielectric investigations of the samples showed that the hyperbranched polyester amide (PEA–OH), both aliphatic and aromatic, have high tendency to adsorb water from the surrounding atmosphere due the presence of the OH groups as terminal groups on the surface. The electric modulus shows that the relaxation response in the modified polymers is not due to the glass transition process since it follows An Arrhenius dependence. In case of aliphatic modified polymer the range of melting separates the trends of dielectric behavior.

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