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Effect of the polymer matrix on the thermal behaviour of a furan-maleimide type adduct in the molten state.

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Summary

The effect of three different polymer matrices on the stability of the exo-adduct formed from N-Phenylmaleimide (PM) and furfuryl alcohol (FAl) toward retro Diels-Alder reaction was studied. First, a stereospecific synthesis of the exo-adduct was carried out at the condensed state and for a best understanding, its thermal properties was reported. The temperature of the rDA reaction of the exo-adduct in polyolefins (a low density polyethylene and a random copolymer of ethylene and glycidyl methacrylate) was found similar to the pure exo-adduct rDA reaction temperature. In a poly(vinylacetate)-g-polycaprolactone matrix this temperature was distinctly lower. In this last matrix, the reversibility of the rDA reaction was proved by the formation of the endo-adduct FAlPM during cooling.

Keywords

Diels-Alder, retro Diels-Alder, N-phenylmaleileimide, furfuryl alcohol, adduct thermal stability, polymer matrix, molten state.

Introduction

Diels-Alder (DA) and retro Diels-Alder (rDA) reactions have been widely used in organic synthesis. Diels-Alder reaction is a reversible 4+2-cycloaddition which involves a diene and a dienophile. It produces an adduct able to convert into reagents at higher temperature.

The furan/maleimide couple is one of the most used diene/dienophile pairs due to the low temperature required for the DA and rDA and the high yield of products. Characterization of adducts, stereoisomers endo/exo structure, kinetic studies of DA and rDA reactions, solvent effect have been reported [1-6]. The temperature at which the rDA reactions occur depends on the specific nature of the reagents in terms of both electronic and steric effects, on the synthesis conditions and reaction mixture for a diene/dienophile pair.

The reversibility of DA has interested the macromolecular field for two or three decades. In order to develop well defined life cycle materials, preparation of reworkable polymers using the DA/rDA reactions becomes more and more investigated. Watanabe et al [6], Teramoto et al [7] obtained linear polymers from bisfunctional diene and dienophile. Liu YL [8], Gandini et al [9], Goiti et al [10-11], Chang BTA et al [12], Jen AKY and coworkers [13] reported the synthesis of thermally reversible crosslinked polymers.

Chen X [14-15] Liu and Hsieh [16] prepared dendrimers from multifunctional diene and dienophile. Organic-inorganic hybrid materials using DA and rDA reactions were synthesized by Adachi et al [17].

More recently Durmaz et al [18] used DA reaction for one pot synthesis of ABC triblocks type macromolecules in mild condition and Costanzo [19] to control dispersion and migration of nanoparticules in polymer matrices.

In all cases, diene and dienophile functions are linked to the macromolecules backbone and most of these synthesis are carried out in solvents. To the best of our knowledge no study was found on the thermal stability of the adducts dispersed or dissolved in a polymer matrix at the molten state.

In the absence of solvent, rDA reaction temperature of solid adduct corresponds to adduct melting temperature. Moreover the reaction occurs with best yield in solid state [5]**.** So, it seemed interesting to study the polymer matrix effect on adduct rDA reaction in the melt.

This article deals with the furan/maleimide type adduct synthesis from furfuryl alcohol and N-phenylmaleimide without solvent and its thermal behaviour in melt polymer matrices with different polarity groups (apolar, semi-polar and polar).

Experimental

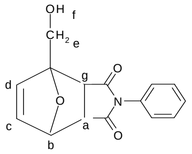
Materials

N-phenylmaleimide (PM) (mp : 87-89°C) and furfuryl alcohol (FAl) purchased from Acros were used without purification. Low density polyethylene, LDPE, PBD 2000® (Tm = 108°C, Mw = 470000 g.mol^{-1}) was supplied by BP, copolymer of ethylene and glycidyl methacrylate Lotader AX8840® (Tm = 103°C ; Mw = 105000 g.mol^{-1}) with 8% wt of glycidyl methacrylate was supplied by Arkema. (PVA-Ac)-g-PCL is a polycaprolactone grafted with a polyvinylalcohol prepared by the partial hydrolysis of acetoxy groups of a poly(vinylacetate) (Tg = 62 °C) [20-21]

Synthesis of furfuryl alcohol/ N-phenylmaleimide endo/exo-adduct (scheme 1)

N-phenylmaleimide (2.5g, 0.014mol) and furfuryl alcohol (1.4g, 0.014mol) were stirred under refluxing at room temperature for 12h. The obtained solid was washed with diethyl ether to afford white powder in endo/exo 71/29 ratio (confirmed by ^{1}H-NMR) with a 66% yield, mp: 118°C (endo), 156°C (exo). ^{1}H-NMR [d$_6$-DMSO, δ (ppm)]: 7.5-7.1 (5H$_{ar}$ endo/exo, m); 6.5-6.6 (2H$_{c,d}$ endo/exo, m,s); 5.2-5.35 (1H$_b$ endo/exo, dd,m); 4.98-5.2 (1H$_f$ endo/exo, m,t); 3.76-4.14 (2H$_e$ endo/exo and 1H$_g$ endo, m); 3.56 (1H$_a$ endo, d); 3.2 (1H$_g$ exo, d), 3.04 (1H$_a$ exo, d). FT-IR (KBr pellet,

cm^{-1}): 3500s (O-H), 3440s (O-H), 3150w (C=C), 3090-3070 (=C-H), 1770m (C=O)sym, 1705vs (C=O)asym, 1592m (C-C phenyl), 1573vw (C=C), 1498 s (C-C phenyl), 1390s (C-N-C)sym, 1177s (C-N-C)asym, 1060m (C-O).



Scheme 1. FAlMP adduct

Synthesis of furfuryl alcohol/ N-phenylmaleimide exo-adduct

N-phenylmaleimide and furfuryl alcohol were mixed together in equimolar quantity at 95°C until a homogen mixture was obtained. Then, the resulting viscous liquid was introduced in an oil bath at 140°C for 8 min. White powder was obtained after washing with diethyl ether with a 82% yield.

mp: 156°C. ^{1}H-NMR [d_6-DMSO, δ (ppm)]: 7.5-7.18 (5H_{ar}, m); 6.58 (2$H_{c,d}$, s); 5.2 (1H_b, s); 4.98 (1H_f, t); 3.75-4.14 (2H_e, m); 3.2 (1H_g, d); 3.04 (1H_a, d). FT-IR (KBr pellet, cm^{-1}): 3504s (O-H), 3450w (O-H), 3150vw (C=C), 3084-3010 (=C-H), 1772m (C=O)sym, 1705vs (C=O)asym, 1592m (C-C phenyl), 1575vw (C=C), 1497s (C-C phenyl), 1393s (C-N-C)sym, 1212s (C-N-C)asym, 1042m (C-O).

Preparation of polymer and exo-adduct blends

All blends were carried out from polymer (87%wt) and exo-adduct (13%wt) in a batch mixer Haake Rheomix model 600 equipped with two counter-rotating blades and a 50 cm^3 mixing chamber. The rotation speed of the rotors was set to 50 rpm and the temperature to 130°C. The polymer was introduced first in the mixing chamber. Then, the adduct was added when torque and temperature were stabilized. After 5 min of mixing, the blend was cooled down at room temperature.

Characterization

Differential scanning calorimetry (DSC) was carried out on a TA instrument Q10 at a heating or cooling rate of 2 to 10°.min^{-1} under N_2 atmosphere. Powder adducts sample of 2 mg were sealed in an aluminium pan. The analysis of polymer samples was started off with heating and cooling scans at 10°.min^{-1} between 0 and 160°C.

Dynamic thermogravimetric runs were made using a Setaram G70 thermal analyser under a dry Helium atmosphere at flow rate of 3L.h^{-1}. Initial weight of the sample was about 60 mg and the heating rate of 10°.min^{-1} .

FT-IR spectra of KBr pellets or polymer films obtained at 120°C under 180 bars for 10 min were recorded on a Nicolet Nexus FT-IR spectrometer in the wave range of 4000-500 cm^{-1}.

^{1}H-NMR spectroscopy measurements were performed on a Bruker Avance spectrometer at 250 MHz with 50% solutions in TCE/C_6D_6 at 80°C for polyolefins and in d_6-DMSO at 25°C for adducts and (PVA-Ac)-g-PCL with tetramethylsilane as internal reference.

Two cycles of heating and cooling between 25°C and 160°C at 1°.min^{-1} were conducted in a well-sealed tube from PM and FAl (1:1) mixture to observe changes in state of the adducts and the addends.

Results and discussion

The main objective of this work is to study the thermal behaviour of the adducts in dispersed or dissolved state in a polymer matrix. For a best understanding, we first study the thermal behaviour of adducts without polymer matrix.

Thermal behaviour of endo/exo-adduct without polymer matrix

As known, the synthesis of furan-phenylmaleimide type adduct at room temperature leads to a stereoisomers mixture with an excess of the endo-adduct (71%). For the first time, the stereospecific synthesis in condensed state of 100% exo-adduct is reported. This DA reaction was obtained in a short time at 140°C and with a good yield (82%). Figure 1 represents the ^{1}H-NMR spectra of endo/exo-adduct in d$_6$-DMSO solution at 25°C, 50°C, 90°C and 120°C. At 90°C, furfuryl alcohol (FAl) and N-phenylmaleimide (PM) characteristics peaks can be observed and prove that rDA reaction occurred. The yield of rDA reaction calculated by NMR results is about 53% at 90°C and 81% at 120°C. The ratio of endo/exo stereoisomers in adduct mixture has changed depending on the temperature. At 50°C the proportion of endo/exo is always 71/29, 29/71 at 90°C and 18.5/81.5 at 120°C. It can be due to possible isomerization of endo-adduct in exo-adduct [1].

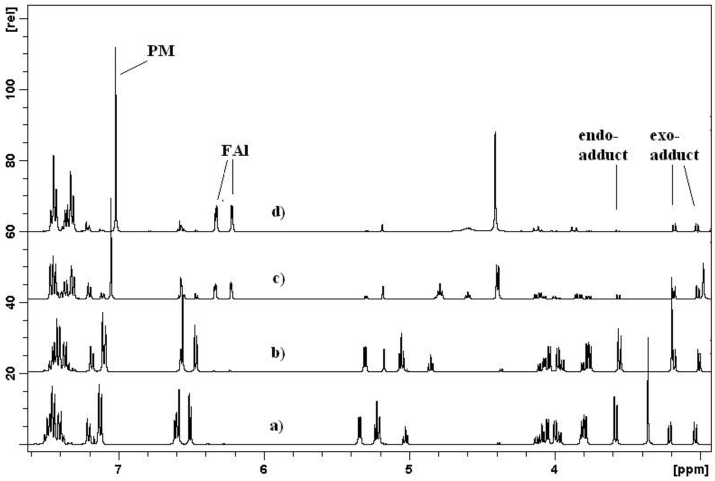


Figure 1: ^{1}H-NMR spectra of endo/exo-adduct in d$_6$-DMSO at 25°C (a), 50°C (b), 90°C (c), 120°C (d).

However, the percentage of exo stereoisomer adduct in the FAl, PM, exo and endo-adduct mixture decreases with increasing temperature proving that rDA reaction in d$_6$-

DMSO occurred with both stereoisomers.

Adducts samples studied by DSC analysis were heated from 0 to 160°C at 2°.min^{-1}, followed by cooling to 0°C at 10°.min^{-1} for several cycles. Figures 2 and 3 show the DSC thermograms of endo/exo and pure exo adducts when heating. In Figure 2 during the 1st heating, two endothermic peaks and an exothermic peak were observed respectively at 118°C, 156°C and 119°C. The peaks observed at 118°C and 119°C in Figure 2 are not present on the DSC thermograms of pure exo-adduct. They may be attributed to the melting of endo-adduct at 118°C and to the endo-exo isomerization and exo-adduct crystallization at 119°C in accordance with Gandini and al [1-2] and Mironov [22]. Peak at 156°C is attributed to exo-adduct melting as we observed change of state in sealed tube at this temperature.

During the following heating cycles (Figure 2), an exothermic peak around 84°C was appeared and the endothermic peak at 156°C was observed again. Both of these peaks decrease with successive scans. During the cooling, no peaks were observed. Pure exo-adduct has the same comportment at similar temperature (Figure 3). The decrease of exothermic and endothermic peaks may be explicated by a possibly decomposition of exo-adduct at temperature higher than 156°C with time.

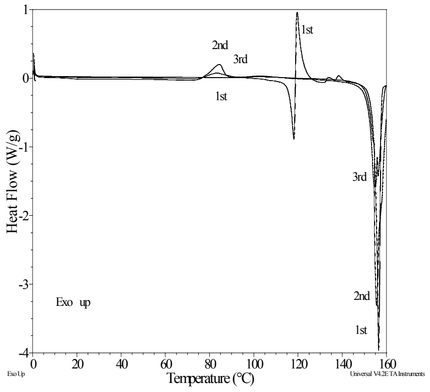


Figure 2. DSC thermograms of the endo/exo-adduct heating cycles

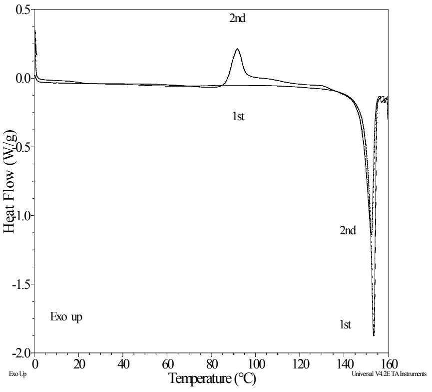


Figure 3. DSC thermograms of the exo-adduct heating cycles

In order to understand the phenomena observed between 115°C and 119°C with the endo/exo-adduct, isothermal run of the endo/exo-adduct at 113°C, 114°C, 116°C and 118°C were carried out (Figure 4). At 113°C, no peak was observed. At 114°C, a broad exothermic peak was observed after about 6 min. At 116°C, the exothermic peak area increases and appears after 2 min. At 118°C, an endothermic peak was appeared before the exothermic peak.

This results suggest that the isomerization can begin near 114°C without endo-adduct melting. At 118°C, adduct melting occurs and seems to catalyse the endo-to-exo isomerization.

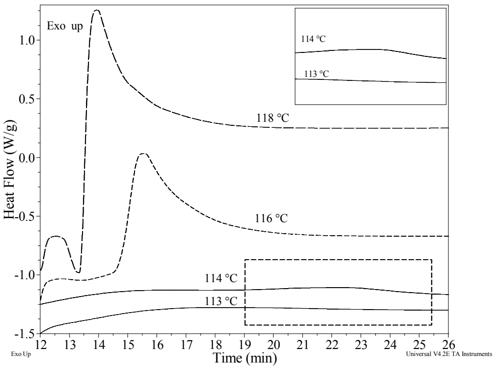


Figure 4. DSC thermograms of the endo/exo-adduct in isothermal runs

Endo/exo-adduct behaviour with increasing temperature was followed by FT-IR in a solid sample cell by keeping the powder between two KBr plates and by increasing temperature from room temperature to 130°C at an average rate of 6°.min^{-1}. Figure 5 represents the FT-IR spectra of adduct recorded at 25°C, 115°C, and 122°C The examination of the spectra shows significantly changes between 115°C and 122°C: intensity of peaks at 3450, 3146, 1180, 1064 cm^{-1} decreases leading to a spectrum comparable to the exo-adduct spectrum. No characteristic peak from FAl and PM was found.

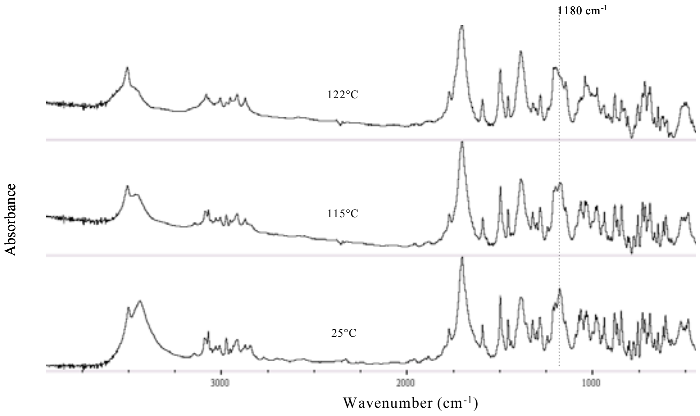


Figure 5. FT-IR spectra of endo/exo-adduct at 25°C, 115°C, 122°C

To test the hypothesis that rDA reaction occurs with melting [5] TGA analysis on adducts were performed. Thermogram recorded in Figure 6 shows the thermal degradation in dynamic run of endo/exo and exo adduct. The first step of endo/exo-adduct thermal degradation begins at 115°C while the thermal degradation in dynamic run of exo-adduct begins near 150°C.

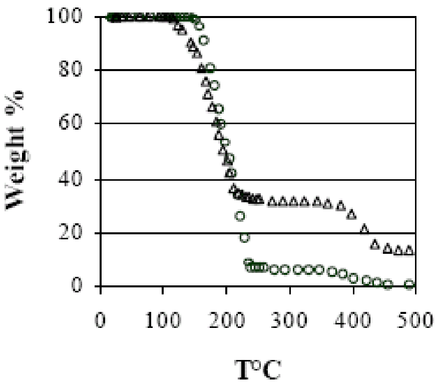


Figure 6a. Dynamic thermogravimetric curves for exo-adduct (○) and endo/exo-adduct (△)

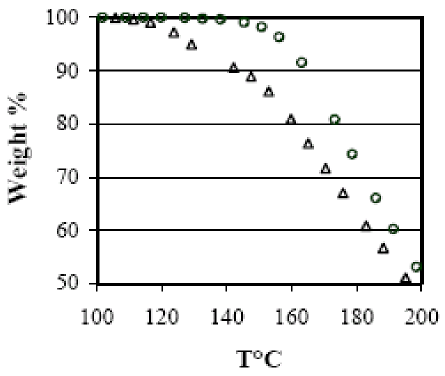
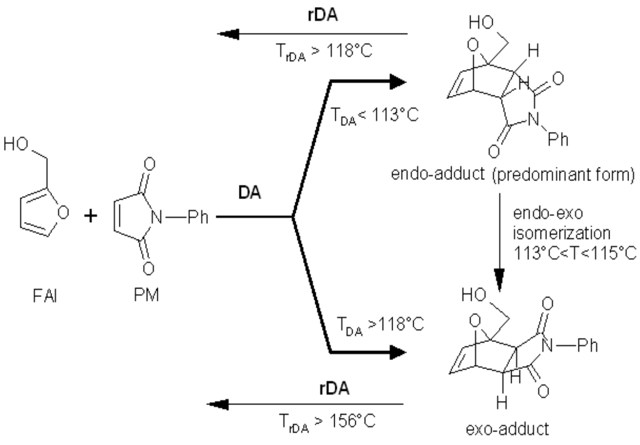


Figure 6b. view of Figure 6a between 100°C and 200°C

These degradation temperatures are similar to the melting endothermic peaks of every adduct. These results confirm that melting and rDA reaction are indivisible in our studies conditions. Our main results on adduct without polymer matrix are represented by Scheme 2. The indicated temperatures correspond to the DSC peaks temperatures.



Scheme 2. DA and rDA reactions and isomerization of adducts.

Thermal behaviour of exo-adduct with polymer matrix

To study the influence of the polymer matrix on the rDA reaction temperature we focused on the exo-adduct for its higher thermal stability at blend temperature and to avoid the isomerization.

DSC thermograms of the exo-adduct blended with polymers are shown in Figure 7.

With Lotader AX8840 and PBD 2000 blends, two endothermic peaks were observed at 108°C and 152°C for PBD 2000, at 103°C and 152°C for Lotader AX8840. With (PVA-Ac)-g-PCL matrix no significant peak was observed. The endothermic peak at 152°C may be attributed to the melting or/and rDA reaction of the exo-adduct. The polymers melting peaks at 103°C for Lotader AX8840 and 108°C for PBD 2000 appeared with a small shoulder near 85°C. This shoulder may correspond to the PM melting temperature formed by rDA reaction during the first heating cycle. The result with (PVA-Ac)-g-PCL suggests that the exo-adduct disappeared or is miscible in polymer.

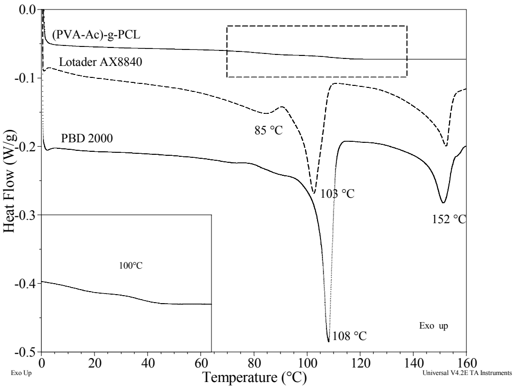


Figure 7. DSC thermograms of FAlMP exo-adduct in several polymer matrices 2nd heating cycle at 2°.min^{-1}.

Figures 8 and 9 represent the comparison of TGA thermograms in dynamic runs of polymers and polymer/exo-adduct blends. Lotader AX8840 and PBD 2000 blends decompose in two main stages. The first stage begins at 140°C and presents a weight loss about 10% at the end of the stage. This step may readily be attributed to the exo-adduct degradation. These result corroborate with the DSC results. Thus exo-adduct dispersed in Lotader AX8840 and PBD 2000 matrices acts like the pure adduct.

Exo-adduct blended with (PVA-Ac)-g-PCL acts differently. Figure 10 shows a degradation beginning near 100°C with a weight loss of 5% at the end of the stage. As (PVA-Ac)-g-PCL includes 1% of water, the right weight loss is of 4% in the blend. If this weight loss is attributed to rDA reaction, then the rDA reaction occurres before the pure exo-adduct rDA reaction and by analogy with our ^{1}H-NMR results (Figure 1), we can conclude that the exo-adduct, and its rDA products FAl and PM, were totally soluble in (PVA-Ac)-g-PCL matrix at the mixing temperature. Therefore, we can suppose that rDA reaction occurred at 130°C during mixing of (PVA-Ac)-g-PCL and pure exo-adduct, leading to formation and volatilization of FAl and PM.

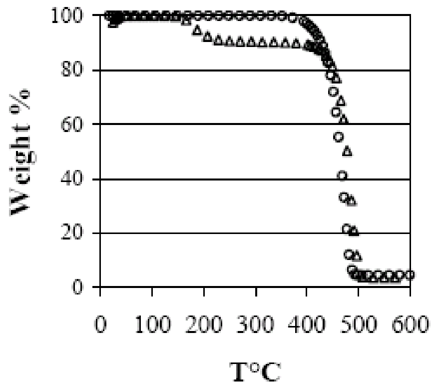


Figure 8. Dynamic thermogravimetric curves of PBD 2000 (○) and PBD 2000/ exo-adduct (△)

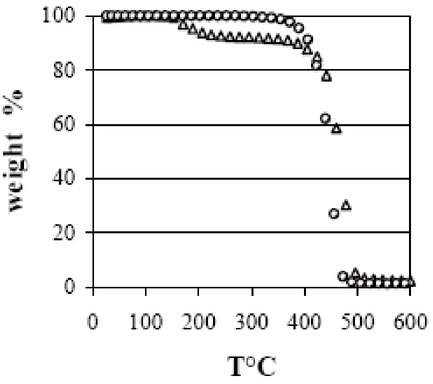


Figure 9. Dynamic thermogravimetric curves of Lotader AX8840 (○) and Lotader AX8840/exo-adduct (△)

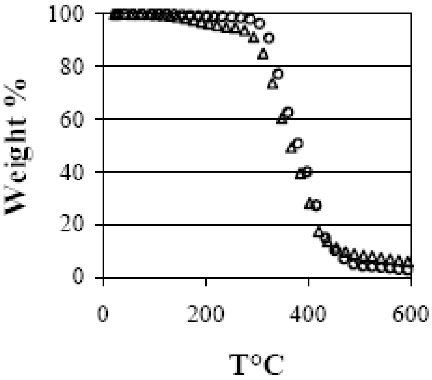


Figure 10. Dynamic thermogravimetric curves of (PVA-Ac)-g-PCL (○) and (PVA-Ac)-g-PCL/exo-adduct (△)

^{1}H-NMR spectra in TCE/C_6D_6 at 80°C of the Lotader AX8840 and PBD 2000 matrices blended with exo-adduct are difficult to analyse because rDA reaction occurred in the NMR tube during the scan. However, they underline that no grafting of adduct occurred for Lotader AX8840/exo-adduct blend. ^{1}H-NMR spectrum in d_6-DMSO at room temperature of exo-adduct blended with (PVA-Ac)-g-PCL (Figure 11) shows endo-adduct and exo-adduct presence in 30/70 molar proportion. Weak intensity peaks of FAl (6.2-6.4, 7.6 ppm) and PM (7.3ppm) are also observed, proving that FAl and PM are not totally volatilizated during the mixing.

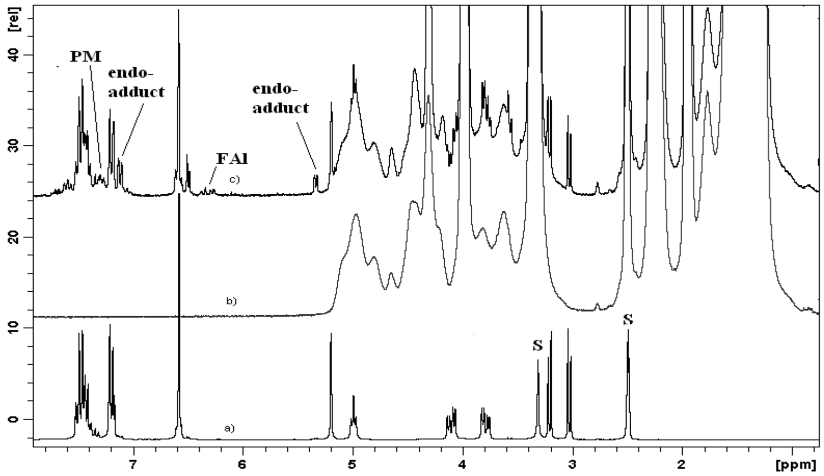


Figure 11. ^{1}H-NMR spectra in d_6-DMSO at 25°C. exo-adduct (a), (PVA-Ac)-g-PCL (b), (PVA-Ac)-g-PCL /exo-adduct (c)

The presence of endo-adduct in polymer matrix is a conclusive evidence of the rDA reaction occurring and its reversibility during cooling. The endo-adduct was formed during the cooling from PM and FAl not volatilized.

Conclusions

Stereospecific DA reaction between N-phenylmaleimide and furfuryl alcohol is realized at condensed state. If at room temperature, a mixture of endo/exo adduct is obtained, pure exo stereoisomer is formed easily at temperature over 118°C. Its thermal behaviour, like decomposition by rDA reaction is closed to melting temperature.

In a polymer matrix in molten state the behaviour of exo-adduct depends strongly on its solubility in the matrix at the mixing temperature. Thus, with miscibility conditions, rDA reaction occurs at temperature lower than exo-adduct melting temperature and leads to endo-adduct formation by DA reaction according to the DA reactions reversibility property. With non miscibility conditions, rDA reaction occurs at exo-adduct melting temperature. So, below this temperature exo-adduct thermal properties are preserved. Further experiments will be performed to verify the reversibility over several cycles of DA reaction with dispersed adduct in a polymer matrix.

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