

Título em Português:	Avaliando Restrições de Mobilidade em Polímeros Usando Ressonância Magnética Nuclear de 1H no Domínio do Tempo
Título em Inglês:	Probing Mobility Restrictions in Polymers Using 1H Time Domain Nuclear Magnetic Resonance
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Uma vez que as coerências de duplo quantum tem relação com a interação dipolar, é possível relacionar o sinal obtido da sequência de duplo quantum com a densidade de spins interagentes por interação dipolar residual (entre núcleos de ^1H localizados em pontos de restrição de mobilidade na amostra). Aplicando essa técnica em temperaturas com a ausência de fase sólida, as coerências podem ser

associadas a emaranhamento ou entrecruzamento de cadeias.

Resultados

Dos polímeros testados, segue abaixo os resultados para a borracha de polibutadieno (PB: $[\text{CH}_2\text{-CH=CH-CH}_2\text{-}]_n$), com seu DQ em função da temperatura

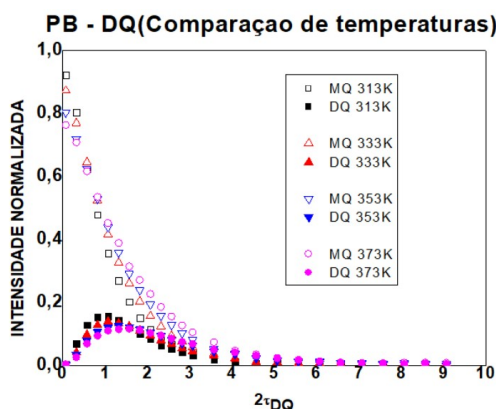


Figura 3: Sinal obtido de DQ para o PB.

Foi possível observar uma queda no sinal com a temperatura, demonstrando a diminuição no grau de emaranhamento para temperaturas maiores. Seguem abaixo também os resultados de DFMSE e DQ para os polietilenos PEX (polietileno $[\text{CH}_2\text{-CH}_2]_n$ entrecruzado quimicamente) e HDPE (polietileno $[\text{CH}_2\text{-CH}_2]_n$ de alta densidade):

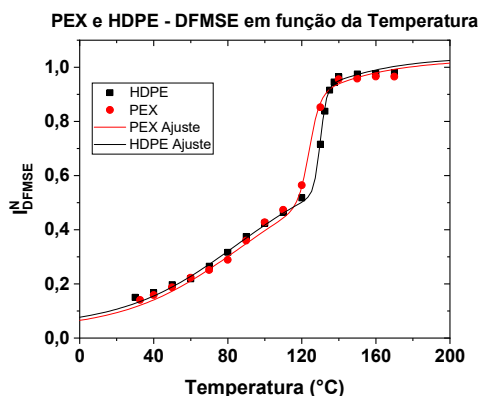


Figura 4: Sinal obtido de DFMSE para PEX e HDPE

É visível que as cadeias estão todas livres por volta de 150°C, e logo a medida de ^1H

DQTDNMR será feito nessa temperatura. Também é visível que os sinais de DFMSE não evidenciam as diferenças entre os polímeros, por outro lado na figura 5, vemos que o PEX possui um maior pico na curva de DQ, mostrando que na ^1H DQTDNMR de fato foram detectados os entrecruzamentos.

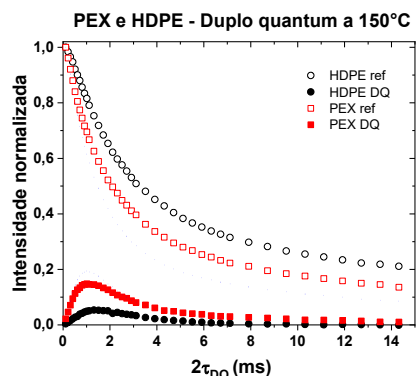


Figura 5: Sinal obtido de DQ para o PEX e HDPE

Conclusões

Foi possível observar que a técnica de DFMSE demonstrou-se eficiente para detectar as temperaturas de transição de mobilidade nos polímeros, no entanto essas transições não evidenciaram diferenças entre os polímeros entrecruzados e não entrecruzados, foi somente possível detectá-las com a técnica de ^1H DQTDNMR, demonstrando sua utilidade e importância, visto a relevância de uma análise precisa desses polímeros que são tão usados pelas indústrias nas mais diversas aplicações.

Referências

- 1-K. Saalwächter. "Proton multiple-quantum NMR for the study of chain dynamics and structural constraints in polymeric soft materials. "Prog. NMR Spectrosc.51.1-35(2007)
- 2-J. Baum and A. Pines, "NMR studies of clustering in solids",J. Am. Chem. Soc. 108. 7447-7454 (1986)
- 3-Jefferson G. Figueiras, Ulison B. Da Silva, Giovani Paro, Marcel N. d'Eurydice, Marcio F. Cobo, Eduardo R. Azevêdo. "Dipolar filtered magic-sadwich-echoes as a tool for probing molecular motions using time-domain NMR". Journal of Magnetic resonance (285) (2017) 47-54

PROBING MOBILITY RESTRICTIONS IN POLYMERS USING ^1H TIME DOMAIN NUCLEAR MAGNETIC RESSONANCE

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Objectives

To establish procedures to analyse temperature profiles obtained by dipolar filtered NMR signals as a way of estimating mobility transitions in constructing polymers.

To establish use ^1H DQTDNMR at low magnetic field to detect local dynamic constrains in constructing polymers.

Materials and Methods

We first employed the DFMSE technique, which involves applying a dipolar filter to the technique known as MSE (Magic Sandwich echoes), as depicted in Figure 1.

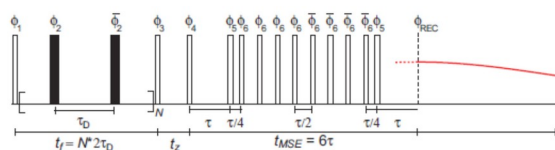


Figure 1: DFMSE Pulse Sequence (ref. 3)

And then, we observe a signal decay profile. If we have a sample that exhibits multiple phases and consequently displays decays with distinct constants associated with each phase, we can select the filter time so that the signal arises solely from the longer decays. This allows us to compare signal intensity at various temperatures and detect mobility transitions, as evidenced by changes in the graph's behavior,

such as abrupt changes in intensity at specific temperatures.

^1H double-quantum nuclear magnetic resonance in the time domain (^1H DQTDNMR) is employed to assess mobility constraints in polymers. The technique enables us to detect the double-quantum coherence curve using the sequence depicted in Figure 2.

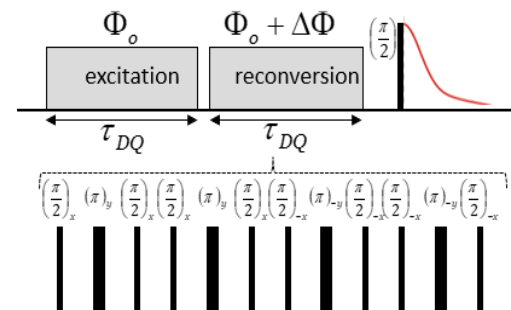


Figure 2: DQ Pulse Sequence (ref. 1,2)

Since double-quantum coherences are related to dipolar interaction, it is possible to correlate the signal obtained from the double-quantum sequence with the density of interacting spins through residual dipolar interaction (among ^1H nuclei located at mobility-restricted points in the sample). By applying this technique at temperatures without the presence of a solid phase, the coherences can be associated with chain entanglement or cross-linking.

Results

Among the tested polymers, here are the results for polybutadiene rubber (PB: $[-CH_2-CH=CH-CH_2-]_n$), with its DQ as a function of temperature:

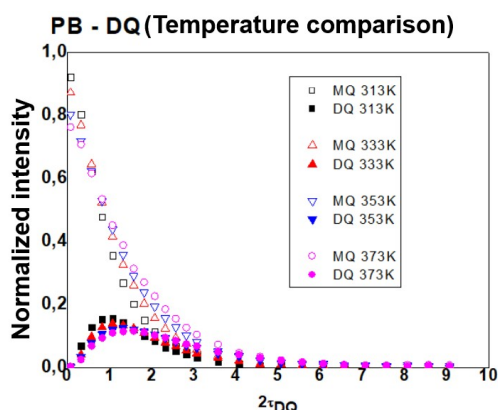


Figure 3: DQ Signal Obtained for PB.

It was possible to observe a decrease in the signal with temperature, demonstrating a reduction in the degree of entanglement at higher temperatures. Below are also the results for DFMSE and DQ for the PEX (chemically cross-linked polyethylene $[CH_2-CH_2]_n$) and HDPE (high-density polyethylene $[CH_2-CH_2]_n$) polymers.

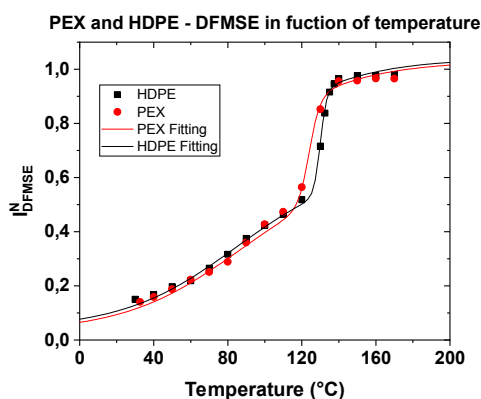


Figure 4: Signal obtained from DFMSE for PEX and HDPE.

It is evident that the chains are all freely mobile around 150°C, and hence, the 1H DQTDNMR measurement will be performed at this temperature. It is also apparent that the DFMSE signals do not reveal the differences between

the polymers. However, on the other hand, in Figure 5, we observe that PEX exhibits a higher peak in the DQ curve, indicating that cross-linkages were indeed detected in the 1H DQTDNMR.

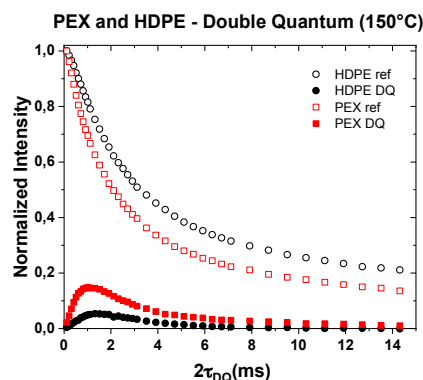


Figure 5: DQ Signal Obtained for PEX and HDPE

Conclusions

It was possible to observe that the DFMSE technique proved efficient in detecting mobility transition temperatures in polymers; however, these transitions did not reveal differences between cross-linked and non-cross-linked polymers. They were only detectable using the 1H DQTDNMR technique, demonstrating its utility and significance, given the importance of precise analysis of these polymers extensively utilized by industries in various applications.

References

- 1-K. Saalwächter. "Proton multiple-quantum NMR for the study of chain dynamics and structural constraints in polymeric soft materials." *Prog. NMR Spectrosc.* 51.1-35(2007)
- 2-J. Baum and A. Pines, "NMR studies of clustering in solids", *J. Am. Chem. Soc.* 108. 7447-7454 (1986)
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