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PRACA DOKTORSKA

Synteza i zastosowanie fluoropolimerów oraz kompleksów lantanowców jako potencjalnych środków kontrastowych ^{19}F MRI

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Abstract

The aim of the study was to design, obtain and test the usefulness of new potential ^{19}F MRI contrast agents. The research included pH-sensitive copolymers and paramagnetic metal complexes. It also focused on the possibility of using the Bloch-Wangsness-Redfield paramagnetic relaxation theory to predict the relaxation properties of paramagnetic ion complexes. The practical application of theoretical calculations was presented on the example of a contrast agent for the detection of copper ions.

The research in the first part of the work involved the use of the ATRP technique to obtain a series of poly($TFEMA_y$-*co*-$HEMA_x$-*co*-$DMAEMA_z$) and poly($HFiPMA_y$-*co*-$HEMA_x$-*co*-$DMAEMA_z$) copolymers with different compositions. HFiPMA copolymers offered approximately five-fold better ^{19}F NMR signal-to-noise ratio compared to TFEMA copolymers with similar fluorine content. It has also been shown that the relaxation times T_1 and T_2 of fluorine nuclei in HFiPMA copolymers depend on the pH of the environment. The reason for this is changes in the conformation of the copolymer chains as a result of the protonation of the tertiary amine group in the DMAEMA.

In the second part of the study, Bloch-Wangsness-Redfield theory was applied to design new ^{19}F MRI contrast agents. It has been shown that correct prediction of the relaxation properties, requires taking into account the electron-nuclear dipole-dipole interactions, the Curie interaction, and in a few cases, the Fermi contact mechanism. In addition, due to the chemical exchange, if the metal has a greater coordination number than the number of ligand atoms involved in the coordination, higher than expected relaxation rates are observed. It leads to lower consistency between the relaxation rates predicted by theory and the observed values.

Convenient methods were proposed to determine the experimental parameters of the theoretical model and potential applications of paramagnetic ions in contrast agents of various types were also proposed. The validity of theoretical considerations was confirmed by designing and obtaining a model responsive ^{19}F MRI contrast agent for the detection of copper ions. The agreement between the predicted and experimental values was shown to be satisfactory and the model can be successfully applied to the design of paramagnetic contrast agents for ^{19}F MRI.