

Volume 15 Number 6 1990

ISSN 0079-6700

54(95)-11

PROGRESS IN
**POLYMER
SCIENCE**

An International Review Journal

Editor: **O VOGL**

*Polytechnic University,
New York, USA*

Associate Editor: **L S CORLEY**

*Shell Development Co.,
Houston, USA*



PERGAMON PRESS Oxford New York
Beijing Frankfurt São Paulo Seoul Sydney Tokyo



RECENT DEVELOPMENTS IN ^{13}C SOLID STATE HIGH-RESOLUTION NMR OF POLYMERS

TONGYIN YU* and MINGMING GUO

Institute of Materials Science, Fudan University, Shanghai, China

CONTENTS

1. Introduction	826
2. ^{13}C CP/MAS NMR technique	827
2.1. The Hamiltonian and the nature of spin interaction	827
2.2. Dipolar interaction and high power proton dipolar decoupling	828
2.3. Chemical shift anisotropy and magic angle spinning (MAS)	829
2.4. ^1H - ^{13}C cross polarization	829
2.5. ^{13}C CP/MAS/DD spectrum	830
3. Polymer chemistry	831
3.1. Pulse sequence for resonance assignment and interpretation	831
3.1.1. Elimination of spin sidebands	831
3.1.2. Quantitative studies	831
3.1.3. Difference in ^1H - ^{13}C transfer rate and variable-contact-time experiment	832
3.1.4. Isolation of protonated and nonprotonated carbon atoms and dipolar dephasing experiment	833
3.1.5. J-coupling and heteronuclear J-resolved ^{13}C NMR in solids	834
3.2. Crosslinked polymers	835
3.2.1. Curing of phenolic resins	835
3.2.2. Curing of epoxy resins	837
3.2.3. Curing of poly(arylene methylene) (PAM) resins	838
3.2.4. Crosslinking of elastomers	839
3.2.5. Radiation crosslinking	841
3.2.6. Other polymer networks	842
3.3. Insoluble linear polymers	845
3.3.1. Chemical composition	845
3.3.2. Hydrogen bonding	845
3.3.3. Solid state reaction	846
3.3.4. Conducting polymers	849
3.4. Structure of other polymer systems	850
3.4.1. Charge transfer complex	850
3.4.2. Polymer composite	852
3.4.3. Surface analysis	852
3.4.4. Insoluble plant polyester	853
3.4.5. Lignin	854

*Author to whom all correspondence should be addressed.

4. Microstructure	854
4.1. Environment effect	855
4.2. Intramolecular conformation	858
4.3. Interchain packing	861
4.4. Conformation in amorphous phase	865
4.5. Conformation in biopolymer systems	867
4.5.1. Poly(amino acids)	867
4.5.2. Starch	868
4.5.3. Cellulose	870
4.6. Variable temperature spectral studies	870
5. Morphology	873
5.1. Experimental method in partitioning ^{13}C resonance of rigid and mobile phases	873
5.1.1. Cross polarization and single pulse excitation	875
5.1.2. Dipolar dephasing experiment	875
5.1.3. Variable-contact-time method	876
5.1.4. $(90^\circ - \tau)_n$ sequence	876
5.2. Partitioning of crystalline and noncrystalline (NC) domain	876
5.3. Degree of crystallinity	878
5.4. Morphology partitioning of chain defects	881
5.5. The third phase	883
5.6. Ionomers and ion-containing polymers	885
5.7. Polymer composites	886
5.8. Orientation	887
5.9. Polymer blends and their miscibility	890
5.9.1. Perturbation in the isotropic chemical shift	891
5.9.2. Intermolecular CP in a mixture of deuterated and protonated materials	892
5.9.3. Determination of relaxation time for the components of a blend	894
5.10. Phase transition	895
6. Summary and outlook	898
References	899

1. INTRODUCTION

As is well known to the chemist, the NMR spectrum of a liquid consists of numerous sharp lines with less than 1 Hz linewidth. This spectrum affords considerable detailed information concerning structure, composition, microstructure, conformation, defects, branching, and in some cases, number-average molecular weights of synthetic polymers. The interaction Hamiltonian in a liquid sample is represented by isotropic chemical shift and scalar spin-spin interaction. All possible anisotropic interactions, namely chemical shift anisotropic, dipole-dipole interaction, etc. are averaged to zero due to the rapid isotropic molecular motion.*

In solid state NMR, however, all these anisotropic interactions remain. In many cases (like ^{19}F and ^1H) dipole-dipole interaction is overwhelming at ordinary magnetic field strength (1–6 Tesla). These result in a more or less bell-like, structureless line shape, from which very little information can be