

Effect of flexibility and cross- linking on crystallization of polymers

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Abstract: Some polymers are studied to know the effect of branching, flexibility and cross – linking on crystallization of polymers. It is found that the chain flexibility of polymers¹ and the velocity of crystal nucleation are important factors .

Keywords: Flexibility , crystalline melting point (T_M) , degree of linearity , molecular architecture , velocity of crystal nucleation , vulcanization , cross – linking , crystallization rate.

Date of Submission: 13-02-2019

Date of acceptance:28-02-2019

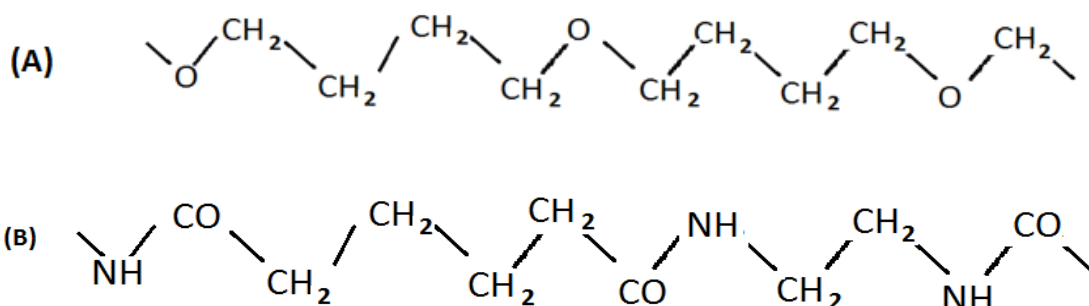
I. Introduction

The physical properties of a polymer , its tendency to crystallize depend upon the molecular architecture as well as the chemical composition. Randomly distributed branches or cross – links can interface significantly with crystallization.

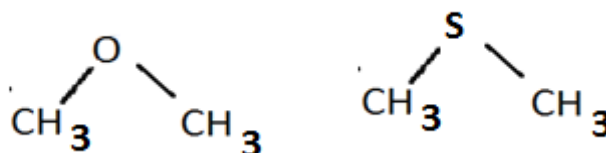
II. Experimental

We examined the physical property crystallization of some polymers : --

- (i) Which differ from linear polyethylene by having groups other than --CH₂--distributed sparsely but regularly along the chain as in examples given below : --



Typical flexibilizing units² are ether oxygen , sulphide sulphurs and ether groups.



- (ii) Which have cross – linking³ either in small amounts or in large amounts.

III. Results And Discussion

- (i) An increase in chain flexibility tends to lower the crystalline melting point(T_M) . The reverse , an increase in chain stiffness , tends to raise the value of T_M

(ii) On the basis of comparison the ease of rotation of methyl groups in dimethyl ethers or dimethyl sulphides with that in ethane.

It is easily observed that due to insertion of the divalent **O** and **S** atom additional room for easier rotation of the **-CH₃-** group are available which increases ease of rotation carries over into polymer chain. Therefore , aliphatic polyethers , polysulphides and polyesters have loer crystalline melting points than that of liner polyethylenes.

(iii) We know that unvulcanised rubber (cis – polyisoprene) has a crystalline melting point above 30⁰C . But when converted it into a network by vulcanization , the rubber cannot crystallizes easily.

The randomly distributed cross – links of course , cannot fit into the lattice of rubber and crystalline melting point (T_M) is somewhat reduced .

The restraints on chain movement exerted by relatively infrequent cross – links affect the velocity of crystal nucleation⁴ and growth more strongly than they affect the thermodynamic equilibrium features .

IV. Conclusion

Those polymers having more chain flexibility have lower value of crystalline melting point (T_M) than less chain flexible polymers. The crystalline melting point also decreases on cross – linking oof polymers. The fact in ease of chain flexibility of polymers are ease of rotation and in case of the cross – linking , it affects the velocity of crystal nucleation.

Acknowledgement

We are very much thankful to the C.D.R.I. Lucknow for the analysis of the samples of polymers

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IOSR Journal of Applied Chemistry (IOSR-JAC) is UGC approved Journal with Sl. No. 4031, Journal no. 44190.

Santosh Kumar " Effect of flexibility and cross- linking on crystallization of polymers." IOSR Journal of Applied Chemistry (IOSR-JAC) 12.2 (2019): 19-20.