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Specific polymer-solvent interaction and stereospecificity of nucleophilic substitution reaction of PVC

G. Martínez, N. Guarrotxena, J. M. Gómez-Elvira, and J. Millán*

CSIC, Instituto de Ciencia y Tecnología de Polímeros, Juan de la Cierva 3, E-28006 Madrid, Spain

SUMMARY

The substitution reaction of PVC with sodium benzenethiolate is studied in a series of solvents in comparison to cyclohexanone as considered in earlier work. As expected from the known influence of solvent on the nucleophile reactivity, the reaction extent is observed to be higher as the solvent polarity increases. In contrast, the stereoselective character of the reaction, as demonstrated for cyclohexanone solution, is found to hold only for solvents containing C=O or -O- function. The others deviate thoroughly from this behaviour. The results are discussed on the grounds of prior findings. They tentatively suggest that the occurrence of the definite conformational changes that are responsible for the stereoselective mechanism, strongly depends on some specific interactions of the solvent with isotactic GTTG$^-$ and heterotactic GTTT triad conformations.

INTRODUCTION

In a series of earlier publications we showed that nucleophilic substitution in Poly(vinyl chloride) (PVC) with sodium benzenethiolate (NaBT) in dilute cyclohexanone (CH) solution proceeds through a stereospecific S_N2 mechanism in that during the fast period of the reaction, the reactive sites lie on the structure **mmr**, the possible conformations of which are GTTG$^-$TT and GTGTTT. These conformations, contain respectively the isotactic GTTG$^-$ and the heterotactic GTTT triad conformation which are the only reactive species. Since all the isotactic and heterotactic triads finished up by reacting under appropriate conditions it was suggested that the mechanism determining factor during the reaction would be the conformational equilibrium -GTTG$^-$TT- $\rightleftarrows$ -GTGTTT- which was thought to provide the highly reactive conformation GTTG$^-$ as long as there exist isotactic sequences (1). Afterwards, the reaction would proceed through the less reactive conformation GTTT in heterotactic parts. Such a mechanism explains satisfactorily the found fact that all the isotactic and heterotactic triads are able to react

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*Corresponding author

even if they are not addopting GTTG$^-$ or GTTT conformations respectively in the virgin polymer. In particular, the highly reactive GTTG$^-$ conformation is known to be little likely (1,2). Further approaches to this mechanism were provided by two recent results. One is that up to conversions of about 7%, the relationship between the decrease of the overall isotactic triad content and the increase of benzenethiolate centred triads was found to be a straight line that passes through the origin and possesses a slope of unity. Thus both processes are concomitant from the very early stages of the reaction. At conversions higher than 7% the slope is less than unity, i.e. structures other than the isotactic GTTG$^-$ conformation start reacting (3). According to our mechanism, these structures are necessarily the GTTT heterotactic conformations. The other result is that as demonstrated by high resolution ^{13}C NMR studies, the specific isotactic triads that are involved during the first stage (up to 7%) are those at the end of isotactic sequences equal to or longer than **-mmmm(r)-** (3).

On the other hand, it should be emphasized that the above results were found to hold for the same reaction in the melt state provided that a certain amount of plasticizer is present (4). In contrast, in the absence of plasticizer the reaction did not exceed conversions of 0.3-0.8% depending on the overall isotactic content of the polymer, just as in solution at reaction temperatures lower than -15°C (1,5).

The whole of the above works strongly suggests that the local changes in conformation, involved in the reaction mechanism are due to that GTTG$^-$ and GTTT conformations, in particular the former one, are of prime importance in both the interaction phenomena and the local mobility of PVC. These features are aimed in a series of current works in our laboratory. One of them deals with the above substitution reaction in a series of solvents in comparison with both CH and plasticizer, as studied previously in solution (3) and in the melt (4,6) respectively. From either the agreement with or the deviations from these behaviours, depending on the type of solvent, some novel ideas as to the relationship between local conformations and specific polymer-solvent interactions, arise straightforwardly, as shown by the preliminary results given in this paper.

EXPERIMENTAL PART

Materials

The PVC sample studied was prepared at 90°C by bulk polymerization. The initiator utilized, azobisisobutyronitrile (AIBN) from Fluka, was recrystallized twice from methanol before use. The number-average molecular weight (Mn= 18,000) was determined at 34°C in CH using a Knauer membrane osmometer.

Dioxane (DI) was refluxed over sodium and distilled from aluminium lithium hydride. Tetrahydrofuran (THF) was distilled under nitrogen with aluminium lithium hydride to remove peroxides inmediately before being used. N-Methylpyrrolidone (MP) was purified by drying over calcium hydride overnight and distillation. N,N-Dimethylformamide (DMF) was dried by adding 10 vol.-% of benzene, which had been dried over calcium hydride. The benzene-water azeotrope was removed by distillation at atmospheric pressure. DMF was purified by shaking with phosphorus pentoxide for four days. Then, it was washed with potassium hydroxide pellets and distilled at 47°C at 14 Torr. The middle fraction of the distilled was used. CH, methyl ethyl ketone (MEK) and hexamethylphosphortriamide (HMPT) were purified by fractional distillation under nitrogen. NaBT was prepared by the reaction of sodium (from Merck) with thiophenol (from Merck) as already described (1).

Substitution reaction with NaBT

The substitution reactions were carried out in the different solvents at 25°C in an atmosphere of purified nitrogen. The full experimental details have been published (1). At suitable intervals, the samples were precipitated in a large excess of methanol. The product was purified from THF into methanol, washed and finally dried under vacuum at 40°C. The degree of substitution was determined by UV spectroscopy (1).

^{13}C NMR spectroscopy

The tacticity of both the starting and modified polymers were measured by means of ^{13}C NMR decoupled spectra obtained at 96°C on an XL-300 Varian instrument, operating at 75.5 MHz using dioxane-d8 as solvent. The spectral width was 2,000 MHz, a pulse repetition rate of 2 sec. and 8K data points were used. The relative peak intensities were measured from the integrated peaks area, calculated by means of an electronic integrator.

RESULTS AND DISCUSSION

The kinetic curves obtained under the same experimental and stoichiometric conditions, for all the utilized solvents are presented in Fig.1. In agreement with expectations, both the fast period rate and the final conversion of the reaction increase with the dipole moment of the solvent that is, with its ability to complex the cation of the nucleophile without solvating the anion appreciably, so that the latter should increase strongly in nucleophility. That well established influence of the solvent on the nucleophile reactant results from that the positive side of the solvent dipole is highly hindered. A typical example is HMPT with its shield of six methyl groups which prevents the anion from solvatation. Note that Fig.1 tells nothing of the influence of solvent on the polymer itself.

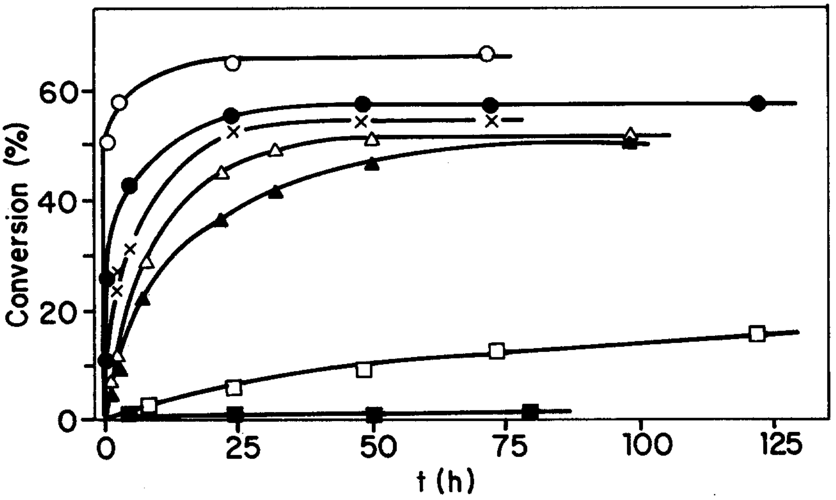

Fig.1. Nucleophilic substitution on PVC with NaBT at 25^{0}C in different solvents. (○) HMPT; (●) MP; (X) DMF; (△) MEK; (▲) CH; (□) THF; (■) DI.

Nevertheless, Fig.2 shows that two solvents, CH and MEK, deviate from the above continuous increase of final conversion with the dipole moment, which suggests that there are two distinct types of solvent effect: one is the above quoted general influence on the nucleophile reactivity; the other is more difficult to understand and, as shown later, should be related to some definite polymer-solvent interations. Which effect predominates in each case depends on the nature of solvent, probably the electron-donor character.

Apart from the kinetics, a crucial point was to elucidate whether the relationship between the decrease in isotactic triads and the increase in modified units, as found both for CH in solution (3) and for dioctyl phtalate (DOP) in the melt (4,6), was influenced by the nature of solvent or not. The answer to this question would not only afford some progress in our conformational mechanism of substitution but could confirm the occurrence

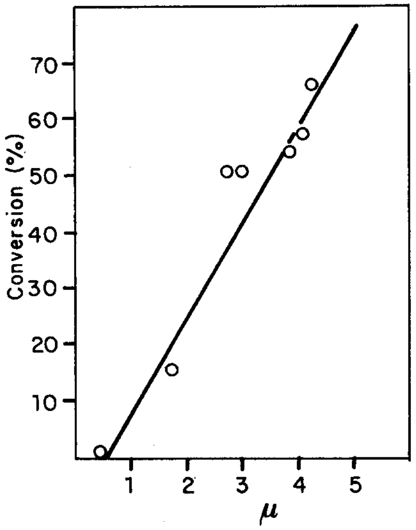

Fig.2.Relationship between maximum degree of substitution (see Fig.1) and the solvent dipole moment (μ).

of specific interaction between local conformations and the solvents as suggested by our current works on both chemical modification and thermal degradation of PVC either in solution or in blends with polymers of various compatibilities (7-9).

A few results are advanced by Fig.3 which compares the prior behaviours to those obtained currently with a series of solvents. Interestingly there are two groups of solvents quite distinct in behaviour. On the one hand MEK and THF just agree with CH and DOP in that two linear behaviours of slope equal to and less than unity respectively are observed. In contrast, MP and DMF exhibit a unique linear behaviour of slope less than unity along the conversions range analyzed so far.

On the grounds of the above quoted recent results (6-9) the former behaviour indicates that only solvents carrying a ketonic or ether group make it likely for the **mm** triads at the end of isotactic sequences no shorter than the heptade **mmmmr(x)**, to addopt the highly reactive GTTG$^-$ conformation. Because GTTG$^-$ content is very low (2-5) that process requires the occurrence of the conformational change

$$\text{-GTGTTT-} \rightarrow \text{-GTTG}^-\text{TT-}$$

until all the above specific **mm** triads have reacted. Now, because GTTG$^-$ conformation is much more unlike than GTGT, that conformational change would account for both, an enhanced interaction between the solvent and GTTG$^-$TT conformation relative to the GTGTTT and the local mobility of the **mmr** segment once it has been complexed by the solvent.

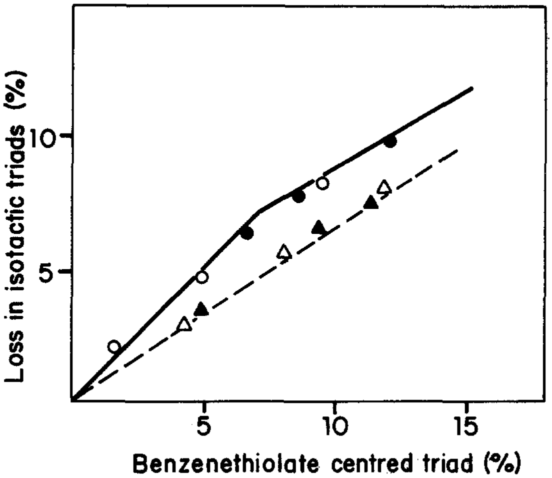

Fig.3. Relationship between benzenethiolate group centred triads and decrease of isotactic triad content. (o) THF; (•) MEK; (▵) DMF; (▴) MP. (—) behaviour with CH and DOP (3,6).

As previously described (3) the change in slope of the linear behaviour as the result of the competing reaction through GTTT conformations in the heterotactic parts indicates that the **mmmr** segments which are capable of undergoing the above conformational change start to disappear. In this connection, the behaviour of the second group of solvents demonstrate that both competing reactions occur from the beginning; hence the interaction between the highly reactive **mmr** segments and these solvents seems to be different in nature from that of the former solvents, so that the above conformational change is, at least to a great extent, disturbed.

The reasons why these differences in polymer-solvent interaction arise are under separate study currently. As a first approximation we are inclined to think that the solvents of the first group exhibit a higher availability of the unshared electron pairs on the oxygen atom, unlike solvents of the second group which possess the resonance-electron donor group -N- . That would cause these groups of solvents to favour respectively electron donor-aceptor interaction and dipole-dipole alignment. At the present state of our work we strongly believe that the electron-aceptor character of methynic proton in PVC increasses markedly from the syndiotactic TTTT triad to the isotactic GTTG$^-$ triad, which is consistent with the interaction polymer-solvent suggested by the results now presented. In fact we showed earlier that acetone is able to extract selectively the PVC parts of higher isotactic GTTG$^-$ conformation content (10).

No matter how preliminary these results are, they confirm the previously proposed influence of local conformations on PVC reactivity and provide some novel ideas about the role of such conformations in the interaction phenomena concerning PVC. Further and more developed results in this field are eagerly expected from the research work presently under way in our laboratory.

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REFERENCES

1. Millán J, Martínez G, Mijangos C (1985) J Polym Sci Polym Chem Ed 23: 1077, earlier references cited therein
2. Millán J, Martínez G, Mijangos C, Gómez-Elvira J M (1989) Makromol Chem Macromol Symp 29: 185
3. Millán J, Martínez G, Jimeno M L (1991) Eur Polym J 27: 483
4. Mijangos C, Gómez-Elvira J M, Martínez G, Millán J (1989) Makromol Chem Macromol Symp 25: 209
5. Martínez G, Mijangos C, Millán J (1985) Polymer Bulletin 13: 151
6. Millán J, Guarrotxena N, Gómez-Elvira J M, Martínez G, to be published
7. Millán J,"Stereospecific control of chemical modification of PVC in condensate state", Invited Lecture, 33rd IUPAC Int.Symp. on Macromolecules, Montreal, Canada 1990
8. Millán J, "Configurational and conformational effects in the thermal degradation of poly(vinyl chloride)", Invited Lecture, III European Polymer Federation Symp. on Polymeric Materials, Sorrento, Italy 1990
9. Millán J, Martínez G, Jimeno M L, Tiemblo P, Mijangos C, Gómez-Elvira J M (1991) Makromol Chem Macromol Symp 48/49: 403
10. Martínez G, Mijangos C, Millán J, Alemany A (1986) Makromol Chem 187: 2649

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