ABSTRACT

π-Electronic Energy Changes in Anionic Polymerization

by

D. B. Hartley and A. Rembaum

The prevalent mechanism of the anionic polymerization system which yields "living polymers" is discussed in terms of a π-electronic energy change. The latter is considered to constitute an approximation of the activation energy of the transition state, and the assumption is also made that the entropy contribution for a series of structurally related compounds remains constant.

The following reaction steps are examined: 1) initiation by electron transfer; 2) dimerization reactions; and 3) anionic propagation.

The LCAO-MO calculations show that the rate of polymerization should be influenced by the type of aromatic initiator used, and this is in agreement with experimental results. Also, the theoretical derivations successfully interpret the stability of hydrocarbon radical anions in contrast to the radical anions of vinyl aromatic monomers which are known to undergo rapid dimerization. Similar arguments predict a low rate constant for the propagation step of 9-vinyl anthracene and acenaphthylene in agreement with recent experimental findings.

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π-Electronic Energy Changes in Anionic Polymerization*

by

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The application of the LCAO MO method to polymerization and copolymerization reactions is relatively recent. It seems that the first paper on this subject was published by Yonezawa, Hayashi, Nagata, Okamura and Fukui[1] who attempted to explain the reactivities of various monomers on the basis of the calculated π-conjugation energy between a monomer and the approaching radical.

A second approach[2] is based on the use of the localization energy concept, the latter being calculated as the difference between the π-energies of the product radical and the monomer.

A third method, which is applied in this paper, consists of evaluating the differences in the π-electronic energies between all products and reactants of a given reaction known to occur in the polymerization process.[3] A comparison of π-energy changes for a series of similar compounds serves then as a reactivity index.

Although a number of organometallic initiators are known to lead to anionic propagation we will limit ourselves to the processes investigated initially by Szwarc[4], et al and later by numerous other scientists.[5]

The action of alkali metals on aromatic hydrocarbons dissolved in tetrahydrofuran or similar solvent gives rise to intensely colored solutions. The primary products of such reactions are hydrocarbon radical anions formed by electron transfer from metal to hydrocarbon. In the

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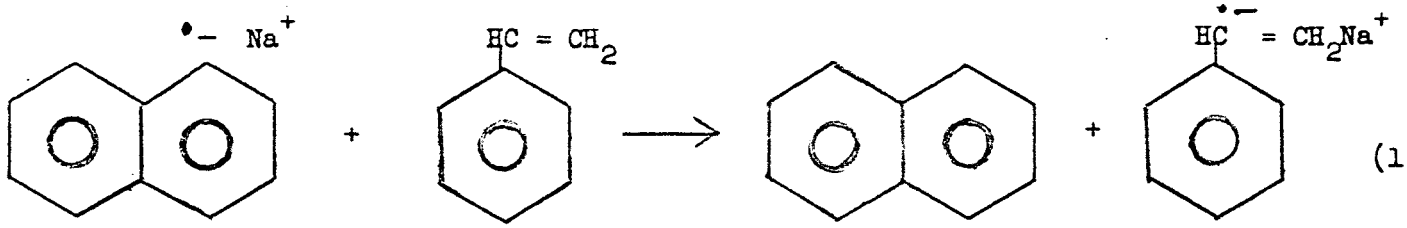
presence of vinyl monomers, initial formation of these highly reactive species can only be inferred since an anionic polymerization reaction occurs leading to polymers which retain their ability to grow and are therefore commonly known as "living polymers."

The initiation is frequently accomplished by an electron transfer from a hydrocarbon radical anion to a vinyl monomer which then undergoes subsequent reactions. The most characteristic reaction steps in this type of polymerization may be presented by the following equations (using naphthalene radical anion and styrene as examples).

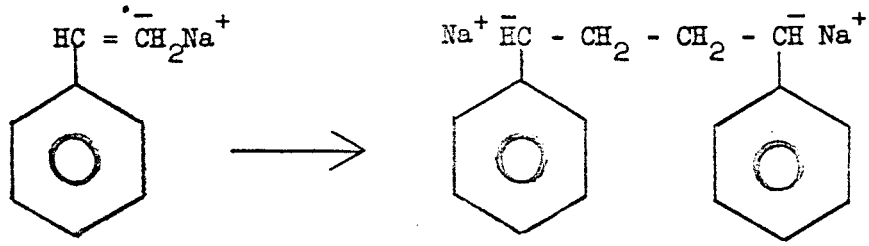
Electron transfer from a hydrocarbon radical anion to monomer. (step 1)



(1)

hydrocarbon radical anion | monomer | hydrocarbon | monomer radical anion

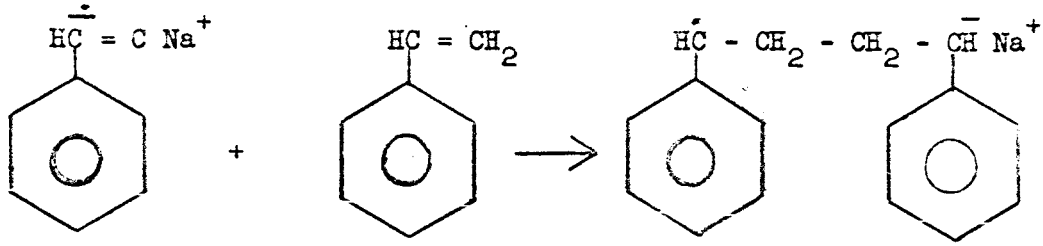
Dimerization of radical anions (step 2)



(2)

monomer radical anion | dimer dianion

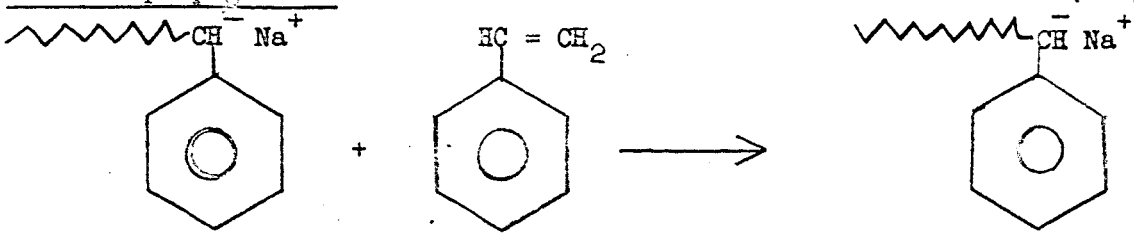
Formation of dimer radical-anions. (step 3)



(3)

monomer radical anion | monomer | dimer radical-anion

Anionic propagation. (step 4)



(4)

polymer anion ("living polymer") | monomer | polymer anion

Apart from the above reactions, chain transfer[6] and formation of complexes[4,7] have been shown to occur and the possibility of other side reactions also exists. However, the above mechanism prevails in many "living polymer" systems and we will examine it in the light of the simple LCAO theory:

The results of the analysis of the π-electronic energies of the reactants and products computed by Hartley, et al[3], on the basis of the approximate molecular orbital theory were found helpful in the correlation and interpretation of most of the known experimental facts. The principles underlying the calculations were based on the following considerations. Examination of the Born-Haber cycle shows that the enthalpy (ΔH) in each of the reaction steps (1), (2), (3), and (4) is equal to the sum of a constant term (independent of the species involved provided these are chemically similar) and the π-energy change associated with the reaction (a function of the particular species).

Since it is unlikely that the entropy CHANGE will vary significantly in a series of reactions involving similar reactants and products, the relative equilibrium position will depend mainly on the ΔH values. Furthermore, as the transition states are presumably similar in a particular series of reactions, the rate constant will differ by virtue of the corresponding activation energies and the latter are assumed to be proportional to ΔH[8]. As it has been established that differences in ΔH arise predominently from the differences in the π-energy changes accompanying the reaction, it is concluded that the reactions in which loss of π-energy is least, will occur faster (in the initial stages when the back reaction is unimportant) and go nearer to completion than in those

reactions in which the loss in π-energy is greater and therefore less favorable to reaction.

Let us assume that either step (1), (2), (3), or (4) is predominant and analyze each one separately.

I. Electron transfer from a hydrocarbon radical anion to monomer (step 1)

This reaction constitutes the first step in the mechanism of some anionic polymerization systems and it was recently proven theoretically and experimentally that it influences the rate of the propagation step[9] as well as the molecular weight distribution.[10]

In Table I are recorded the π-electronic energy changes in terms of the resonance integral β for a series of hydrocarbon radical anions which may be used as initiators for the polymerization of styrene. The coefficients of β of the lowest antibonding orbital, also included in Table I, have been found to offer correlations with polarographic reduction potentials* and electron affinity. Also the decrease of the absolute values of the coefficients on moving down the column reflects the increasing tendency to accept an electron from an alkali metal.

*See, for example, Hoijtink, G. J., Rec. Trav. Chim. 74, 1525 (1955) and Matsen, F. A., J. Chem. Phys. 24, 602 (1956). For a complete description of recent correlations between the energies of highest filled and lowest empty molecular orbitals and polarographic oxidation reduction potentials see "Molecular Orbital Theory for Organic Chemists," by Streitwieser, A., Jr., J. Wiley and Sons, New York, 1961.

TABLE I

Initiation of the Polymerization of Styrene by Electron Transfer; (step 1)

π-Energy Changes in the Reaction;

Hydrocarbon Radical Anion + Styrene $\longrightarrow$ Hydrocarbon + Styrene Radical Anion

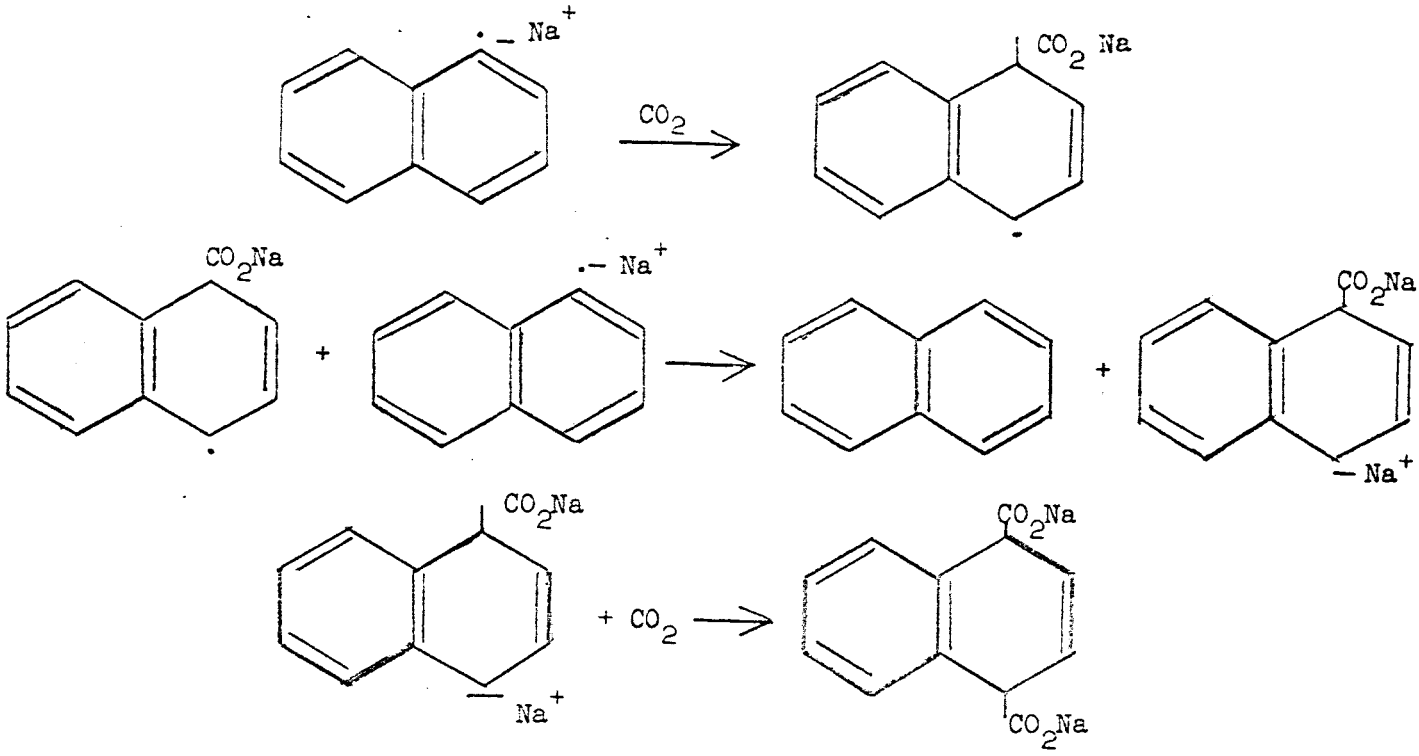
Radical anion	Change in π-energy in units of β	Coefficient of β of the lowest antibonding orbital
Benzene	+0.338	-1.000
Biphenyl	+0.042	-0.705
Naphthalene	-0.044	-0.618
Phenanthrene	-0.0579	-0.605
1,1-Diphenylethylene	-0.098	-0.564
Stilbene	-0.158	-0.504
Anthracene	-0.248	-0.414
1,4-Diphenylbutadiene	-0.276	-0.386
Tetraphenylethylene	-0.294	-0.368
Perylene	-0.315	-0.347
Tetracene	-0.367	-0.295
Acenaphthylene	-0.377	-0.285

The rate of polymerization is greatly influenced by the type of aromatic initiator used. This is in agreement with recent experimental findings which show that the order of catalytic activity of condensed aromatic hydrocarbon radical anions toward polymerization of acrylonitrile, styrene and isoprene is: naphthalene > anthracene > tetracene > pentacene [9].

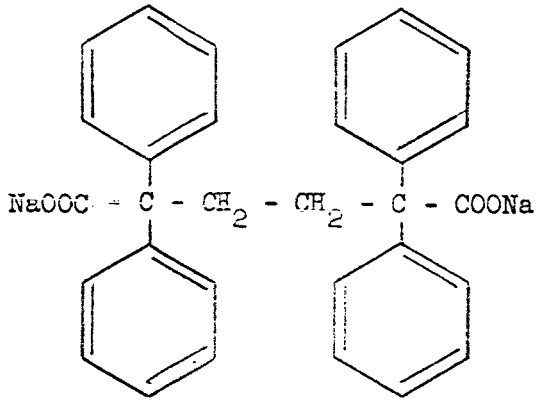
The change of π-energy (Table I) which is assumed to be proportional to ΔH indicates that the transfer of an electron would occur faster from a biphenyl radical anion to styrene than from a naphthalene radical anion. This was shown to be experimentally true[10] and similar reasoning was used by Kawazura[9] to explain the extreme slowness of polymerization of styrene and isoprene by means of the naphthacene radical anion. (Possibility of complex formation should however not be overlooked, particularly with highly condensed aromatic radical anions such as anthracene or naphthacene.)

II. Dimerization of radical anions (step 2)

A number of radical anion systems have been studied and sufficient evidence has been accumulated to indicate in most cases whether the monomeric radical anion or dimeric dianion is the more stable species in solution. Thus it is now well established that naphthalene, biphenyl and anthracene form radical anions which do not dimerize and whose electron spin resonance spectra remain unchanged for long periods of time.[19] Moreover, on treatment with water, alcohol or carbon dioxide, these systems yield the unchanged hydrocarbon plus monomeric dihydro derivatives. The mechanism of carboxylation of the naphthalene radical anion, for example, was postulated to be as follows:[11]



The formation of the 1,2 isomer obeys an identical mechanism which is in agreement with the experimental facts. In contrast to the above the carboxylation of a solution of sodium 1,1-diphenylethylene under identical conditions as used for naphthalene, yields the sodium salt of 1,1,4,4-tetraphenyl butane-1,4-dicarboxylic acid (I)[12].



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If, on the other hand, solutions of sodium styrene or sodium α-methyl styrene are treated with methanol or carbon dioxide, high molecular weight polymers are isolated. Attempts to obtain an ESR signal from styrene[13],

butadiene and isoprene[14], during their anionic polymerizations were not successful. Recent polymerization studies demonstrate that the radical anions of 4-vinyl biphenyl and β-vinyl naphthalene undergo rapid dimerization and polymerization and like styrene do not exhibit ESR signals at room temperature. However, acenaphthylene, α-vinyl naphthalene[20] and 9-vinyl anthracene, under identical experimental conditions, yield well-resolved ESR spectra which persist throughout the anionic polymerization process. These facts have not been explained in a satisfactory manner heretofore.

The reason for the high stability of radical anions of unsubstituted aromatic systems in contrast to some vinyl monomers becomes immediately apparent on examination of the π-energy changes recorded in Table II, which also summarizes most of the known experimental data.

Table II demonstrates a good correlation between the π-energy changes accompanying dimerization and the nature of the more stable species observed in solution. In particular, the differences in behavior of vinyl aromatic radical anions and those of condensed ring compounds are satisfactorily interpreted on an energetic rather than a steric basis.

The π-energy loss for the dimerization of N-vinylcarbazole was recently found to be equal to 2.710β, i.e. a value intermediate between 9-vinylanthracene and anthracene, and it is indeed gratifying to find that N-vinylcarbazole does not dimerize to any significant extent when reacted with sodium under identical conditions as the hydrocarbons of Table II[18].

A further point which warrants attention is the possibility of two different radical anions combining, in a manner similar to that discussed above, to form a mixed "dimer." Obviously any radical anion which normally dimerizes would be expected, on the basis of the figures of Table II, to be energetically capable of combining with a radical anion

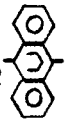
TABLE II

Dimerization of Radical Anions; π-Energy Change in the Reaction;

2 Monomer Radical Anions $\longrightarrow$ Dimer Dianion (step 2)

Radical anion	Nature of stable species	π energy loss in units of β
1,1-Diphenylethylene	anionic dimer	1.900
Styrene	anionic dimer	2.083
4-Vinylbiphenyl	anionic dimer	2.222
1-Vinylnaphthalene	anionic dimer + radical anion	2.271
2-Vinylnaphthalene	anionic dimer + radical anion ?	2.276
9-Vinylanthracene	anionic dimer + radical anion	2.363
Anthracene	radical anion	3.197
1,4-Diphenylbutadiene	radical anion	3.267
Tetracene	radical anion	3.270
Stilbene	radical anion	3.307
Naphthalene	radical anion	3.360
Phenanthrene	radical anion	3.384
Biphenyl	radical anion	3.390
Perylene	radical anion	3.584
Acenaphthylene	radical anion	3.678
Tetraphenylethylene	radical anion	4.102

higher in the series. Such "heterodimerization" would of course occur most readily when the respective radical anions were formed together (e.g., by common transfer from sodium biphenyl) in momentarily high concentration.

Moving down Table II, anthracene is the first radical anion which does not dimerize to any measurable extent. In the presence of styrene radical anions, however, the heterodimerization π-energy loss is considerably reduced, i.e., to $2.640\beta = 1/2\ (2.083 + 3.197)$, perhaps sufficiently to allow the reaction to take place when anthracene and styrene are both present as, for instance, when sodium anthracene is used to initiate styrene. The conditions are reproduced exactly in an experiment recently reported by Szwarc[11] who indeed finds a "complex" formed between styrene and anthracene, having one "dormant" living end. According to the present interpretation, this would have the structure PhCH-CH_2-  -, a possibility recognized by Szwarc.

If such a "dimer" is formed with styrene radical anion, a similar reaction should also occur between the radical anions of anthracene and 1,1-diphenylethylene, and perhaps between 4-vinylbiphenyl and the vinylnaphthalene radical anions.

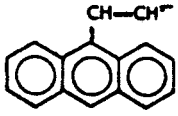
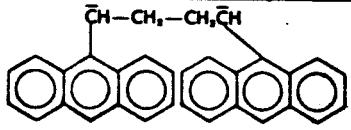
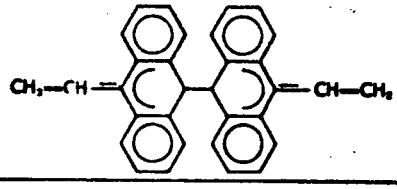
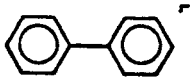
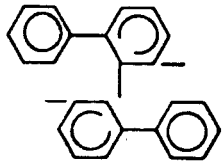
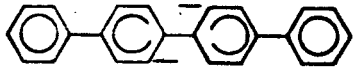
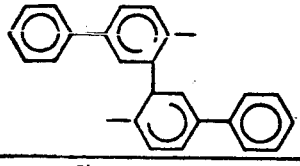
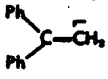
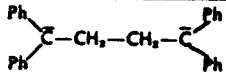
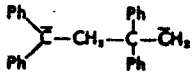
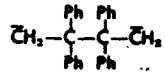
Another pertinent problem of the dimerization reaction is the structure of the dimer obtained. This can also be predicted on the basis of the calculated π-energy.

Table III shows the expected relative stability of some dimers of selected radical anions. Where the structure of the dimer has been proven experimentally, it is found to agree with the predictions made here.

Thus 2,5 diphenyl adipic acid is formed by carboxylation of sodium styrene, and 1,1 4,4 tetraphenyl butane by hydrolysis of sodium 1, 1 diphenyl ethylene[12, 15].

TABLE III

Structure and π-Energy of Some Dimer Dianions

Radical anion	Dimer	π-Energy of dimer in units of β
Ph—CH=CH⁻ Styrene	PhC̄H—CH₂—CH₂—C̄HPh	17.441
	PhC̄H—CH₂—CHPh—C̄H₂	16.721
	C̄H₂—CHPh—CHPh—C̄H₂	16.000
 9-vinylanthracene		40.530
		39.739
 Biphenyl		27.967
		27.873
		27.679
 1,1-diphenylethylene		34.601
		33.301
		32.000

III. Formation of dimer radical-anions (step 3)

Though the rate constant of dimerization of two radical anions may be larger than that of addition of a radical anion to a vinyl monomer (Eq. 3), in general the generator is present in excess, and the rate of the latter process may therefore exceed that of the former[16]. It is therefore of interest to estimate the expected order of increasing rate of addition in a series of aromatic hydrocarbons. This has been done in Table IV, where the radical anions most likely to add their own monomer head the series.

Tables III and IV thus summarize the main energetic factors to be considered in discussing dimerization of radical anions by the two alternative mechanisms (Eqs. 2 and 3). Both processes have been demonstrated to occur in the case of α-methylstyrene. While it has not proved possible theoretically to say which of the two possible mechanisms will occur in a given instance, it is to be noted from the tables that radical anions showing a high tendency to dimerize by the reaction represented by step 2 (Eq. 2) also show the most marked tendency to form the dimeric ion by the alternative reaction (Eq. 3). The fact that the radical anions heading the two tables have been demonstrated to dimerize experimentally bears out the theoretical results. Exceptional perhaps is the case of the 9-vinylanthracene radical anion which should exhibit a marked tendency to add its own monomer. The experimental evidence accumulated so far is insufficient to confirm this prediction.

TABLE IV

Expected Order of Reactivity of Hydrocarbon Radical Anions to Generator; (step 3)

(Monomer Radical Anion + Monomer $\longrightarrow$ Dimer Radical-anion)

Radical anion	energy loss* in units of β
1,1-Diphenylethylene	2.464
9-vinylanthracene	2.706
Styrene	2.745
1-vinylnaphthalene	2.770
4-vinylbiphenyl	2.786
2-vinylnaphthalene	2.822
Tetracene	3.565
Anthracene	3.611
1,4-Diphenylbutadiene	3.653
Stilbene	3.811
Perylene	3.931
Acenaphthylene	3.963
Naphthalene	3.978
Phenanthrene	3.989
Biphenyl	4.095
Tetraphenylethylene	4.470

*Tail-to-tail configuration assumed.

V. Anionic Propagation (step 4)

Of perhaps greater interest is the estimation of π-energy changes accompanying propagation of anionic polymerization of the monomers under consideration because the same type of arguments employed in discussing dimer formation should indicate an order of polymerizability.

The anions originating from the monomers listed in Table V are expected to propagate with increasing difficulty as we move towards the bottom of the table. Preliminary investigations[6] indicate that this is indeed the case. The absolute rate constant (k_p) for the propagation step in the anionic polymerization of styrene has been found to be of the order of 500 ℓ/(mole sec),[4] while recent studies show that k_p for 9-vinyl anthracene and acenaphthylene, polymerized under identical conditions as styrene, is of the order of 2×10^{-1} and 10^{-4} ℓ/(mol sec), respectively. Only low molecular weight polymers were obtained and a study of polymerization rates of these monomers as a function of temperature yielded relatively high activation energies. This is consistent with the theoretical deductions.

The results of Table V should also apply to free radical and cationic polymerization. Since no experimental determinations of propagation rate constants are available for these systems no comparison between theoretical and experimental results can be made at present.

TABLE V

Anionic Polymerization: π-Energy Changes in the Reaction;

Polymer Anion ("living polymer") + Monomer $\longrightarrow$ Polymer Anion (step 4)

Monomer	π energy loss in units of β
Styrene	2.424
β-vinylnaphthalene	2.428
4-vinylbiphenyl	2.432
α-vinylnaphthalene	2.447
9-vinylanthracene	2.477
1,1-diphenylethylene	2.815
Acenaphthylene	2.936

As the π-energy loss in the propagation step (Table V) represents the exothermicity of the reaction, the latter is expected to decrease moving down the column of Table XII-10. The finding that the polymerization of acenaphthylene proceeds with a considerable evolution of heat[17] is inconsistent with the results of Table V. It should be borne in mind that the data recorded in Tables I, II, III, IV, and V presume that the rate-determining step is either (1), (2), (3), or (4). This is frequently not the case, which may account for some discrepancies, while others may be due to the fact that the entropy changes accompanying the formation of the transition state are not always similar.

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