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Solution and solid-state polymerizations of substituted *p*-quinodimethanes and *p*-quinone methides

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Abstract

This article describes the polymerization behavior of electron-accepting and electron-donating *p*-quinonoid monomers such as substituted *p*-quinodimethanes and *p*-quinone methides in solutions and solid states. In the solution polymerizations, the electron-accepting substituted *p*-quinodimethanes and *p*-quinone methides with same substituents such as cyano, ester, and sulfonyl groups at the exocyclic positions are not homopolymerizable, but copolymerizable with donor monomers like styrene in an alternating fashion. Their spontaneous polymerizations with donor monomers have been explained with the bond-forming initiation mechanism. The substituted *p*-quinodimethanes with ester groups are a first example to show an amphoteric behavior in alternating copolymerizations. Some electron-accepting substituted *p*-quinodimethanes and *p*-quinone methides with different substituents such as cyano, ester, acyl, alkylthio, and/or phenyl groups are homopolymerizable, and an anionic polymerization initiated with a butyllithium initiator proceeded in a living manner. Equilibrium polymerization behavior have been found in their radical homopolymerizations, and on the basis of the thermodynamic parameters determined for their polymerizations, it has been concluded that homopolymerizabilities of the electron-accepting substituted *p*-quinodimethanes and *p*-quinone methides are determined exclusively by a steric hindrance effect arising from the substituents at the exocyclic positions. A new concept for the radical alternating copolymerization have been proposed on the basis of the change in modes (random and alternating copolymerizations) for their copolymerizations with styrene and the cross-propagation step analysis by linear free energy relationship. The polymerizations of the electron-donating substituted *p*-quinodimethanes take place only in the presence of oxygen molecules. In the solid-state polymerizations, some electron-accepting substituted *p*-quinodimethanes with same ester substituents polymerized topochemically in vacuo, and the strict requirements of topochemical polymerization for substituted *p*-quinodimethane and *p*-quinone methide monomers have been determined on the basis of their crystallographic data. Topochemical alternating copolymerization with molecular oxygen in solid state was discovered for the first time.

Keywords: *p*-Quinodimethanes; *p*-Quinone methides; Polymerization behavior

1. Introduction

Polymerization of unsubstituted *p*-quinodimethane proceeds by opening one double bond and a formation of a single bond in the same way that like as ethylene forms a poly(ethylene) (Scheme 1). However, an energy difference (33–38 kJ/mol) [1] between a quinonoid ground state (singlet ground state) and a benzenoid transition state (triplet excited state) for the *p*-quinodimethane monomer is much smaller than the corresponding value (343 kJ/mol) [2] for the ethylene one. Therefore, the unsubstituted *p*-quinodimethane is highly reactive compared to ethylene and polymerizes spontaneously even at temperature as low as −78 °C. This unusually small energy difference provides extremely high reactivity to the unsubstituted *p*-quinodimethane [3] and it is difficult to isolate it as a pure monomer under normal conditions. If it is difficult for the *p*-quinodimethane to take the benzenoid structure, they become less reactive because the excitation energy level, that is, the energy difference becomes larger [4]. Introduction of electronegative atoms or electron-withdrawing groups to the exocyclic positions (7 and 8 positions) decreases the aromaticity of the benzenoid structure, leading to the stabilization of *p*-quinodimethanes.

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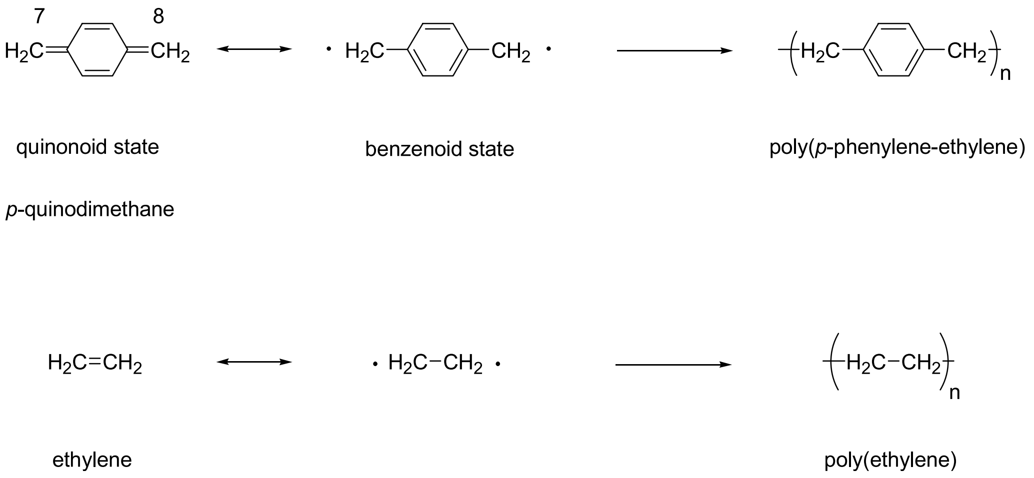


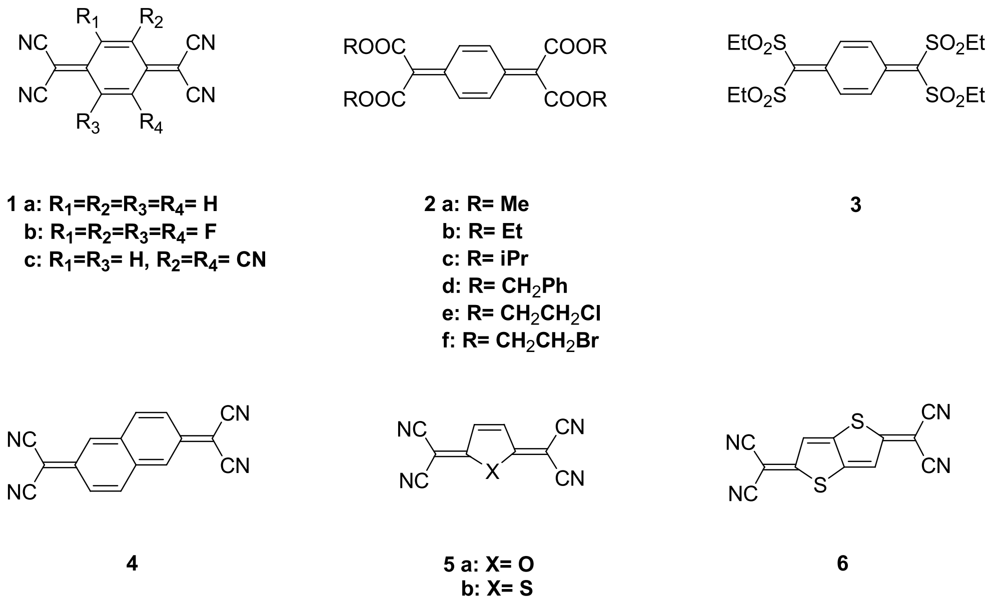
Scheme 1.

p-Benzoquinone with more electronegative oxygen atoms (O) compared to carbon atoms (CH_2), and 7,7,8,8-tetracyanoquinodimethane (**1a**), 7,7,8,8-tetrakis(methoxycarbonyl)quinodimethane (**2a**), and 7,7,8,8-tetrakis(ethylsulfonyl) quinodimethane (**3**) with the electron-withdrawing substituents such as cyano, ester, or sulfonyl groups at 7 and 8 positions are the case. *p*-Quinodimethanes are regarded as highly conjugative stabilized monomers rather than ethylene from the comparison in their chemical structures, and also the substitution of the hydrogen atoms at the exocyclic carbons with electron-withdrawing substituents may contribute to further stabilization of the substituted *p*-quinodimethanes. Therefore, the substituted *p*-quinodimethanes, isolable as pure crystalline and highly conjugative (reactive) monomers, are expected to show new and unique polymerization behavior beyond the scope of the conventional polymer chemistry established on the basis of the polymerizations of vinyl monomers. In this article will be described the polymerization behaviors in solutions and in solid states for isolable *p*-quinonoid monomers such as the substituted *p*-quinodimethanes and substituted *p*-quinone methides.

2. Solution polymerizations of electron-accepting or electron-donating *p*-quinonoid monomers

2.1. Electron-accepting substituted *p*-quinodimethanes with same substituents

A series of new substituted *p*-quinodimethanes with strong electron-accepting properties such as 7,7,8,8-tetracyanoquinodimethane (**1a**) [5], 7,7,8,8-tetrakis (methoxycarbonyl)quinodimethane (**2a**) [5], 7,7,8,8-tetrakis(ethylsulfonyl)quinodimethane (**3**) [6], and



1 a: R_1=R_2=R_3=R_4= H
b: R_1=R_2=R_3=R_4= F
c: R_1=R_3= H, R_2=R_4= CN

2 a: R= Me
b: R= Et
c: R= iPr
d: R= CH_2Ph
e: R= CH_2CH_2Cl
f: R= CH_2CH_2Br

3

4

5 a: X= O
b: X= S

6

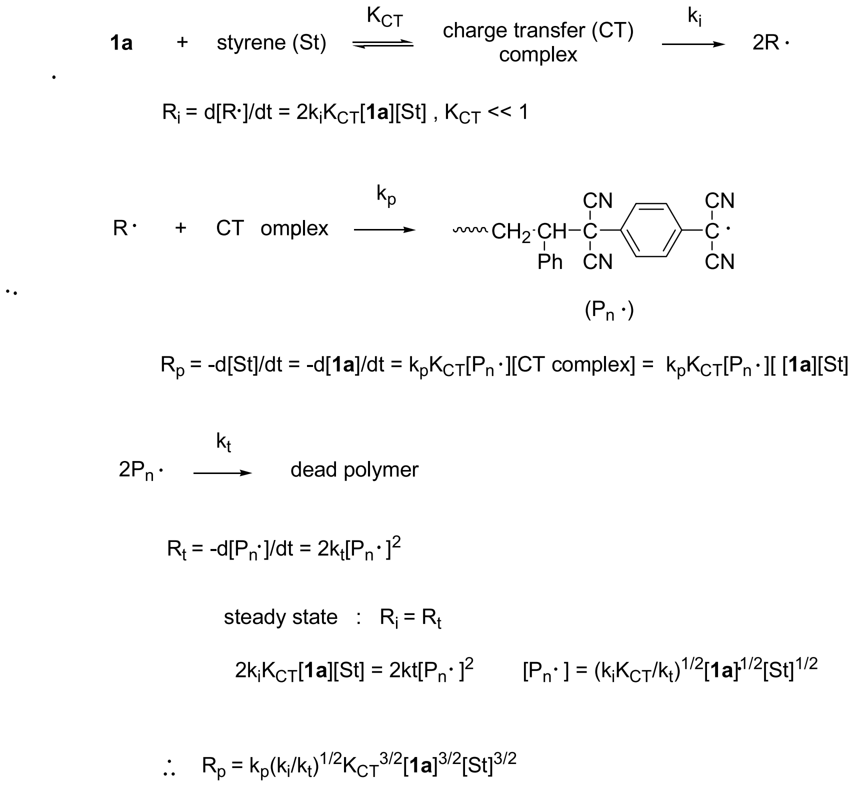
Chart 1.

Table 1
Rate constants (k_p), overall activation energies (E_a), and half-life time ($t_{1/2}$) for the copolymerizations of the **1a**-styrene, **1b**-styrene, **1c**-styrene, and **4**-styrene systems

System	Kinetic order	$k_p \times 10^3$ ($L^{1/2}$ $mol^{-1/2}$ s^{-1})	Temp. (°C)	E_a[a] (kcal/mol)	$t_{1/2}$ (min)
1a-Styrene	1.5	2.75	34.5	17.3	1000[b]
4-Styrene	1.5	21.4	34.5	16.3	151
1b-Styrene	1.5	529	34.5	16.6	4
1c-Styrene	1.0	5.05[c]	10	16.7	1.2

[a] 1 cal = 4.18 J.
[b] Calculated from rate constants.
[c] In s^{-1}.

11,11,12,12-tetracyano-2,6-naphthoquinodimethane (**4**) [7] were synthesized as pure isolable crystals at room temperature in the early 1960s. 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (**1b**) [8] and 2,5,7,7,8,8-hexacyanoquinodimethane (**1c**) [8] were reported later in 1975. Furan, thiophene, and thieno[3,2-b]thiophene analogues of the electron-accepting substituted *p*-quinodimethanes, 2,5-bis(dicyanomethylene)-2,5-dihydrofuran (**5a**) [9], 2,5-bis(dicyanomethylene)-2,5-dihydrothiophene (**5b**) [10], and 2,5-bis(dicyanomethylene)methylene-2,5-dihydrothieno[3,2-b]thiophene (**6**) [11], have been also synthesized (Chart 1). These electron-accepting substituted *p*-quinodimethanes have been extensively studied in connection with their charge-transfer complexes showing high electric conductivities, after referred to as organic metals [9,11–13]. In 1978, we reported a spontaneous alternating copolymerization of **1a** with styrene for the first time, where **1a**, known as a polymerization inhibitor, can act as an acceptor monomer in the copolymerization [14]. The copolymerization of **1a** with styrene in acetonitrile at 40 °C gives pink-colored powers (intrinsic solution viscosity of 0.407 dl/g in *N,N*-dimethylformamide (DMF)) with a perfect alternating structure, determined by pyrolysis gas chromatography with a high-resolution glass capillary column [15]. All other substituted *p*-quinodimethanes in the Chart 1 copolymerize alternatingly with styrene in the presence and absence of 2,2′-azobis(isobutyronitrile) (AIBN) to give the corresponding alternating copolymers, and these behave as acceptor monomers like **1a** [16–23]. From the kinetic studies of



Scheme 2.

Table 2
Polymerization modes in acetonitrile

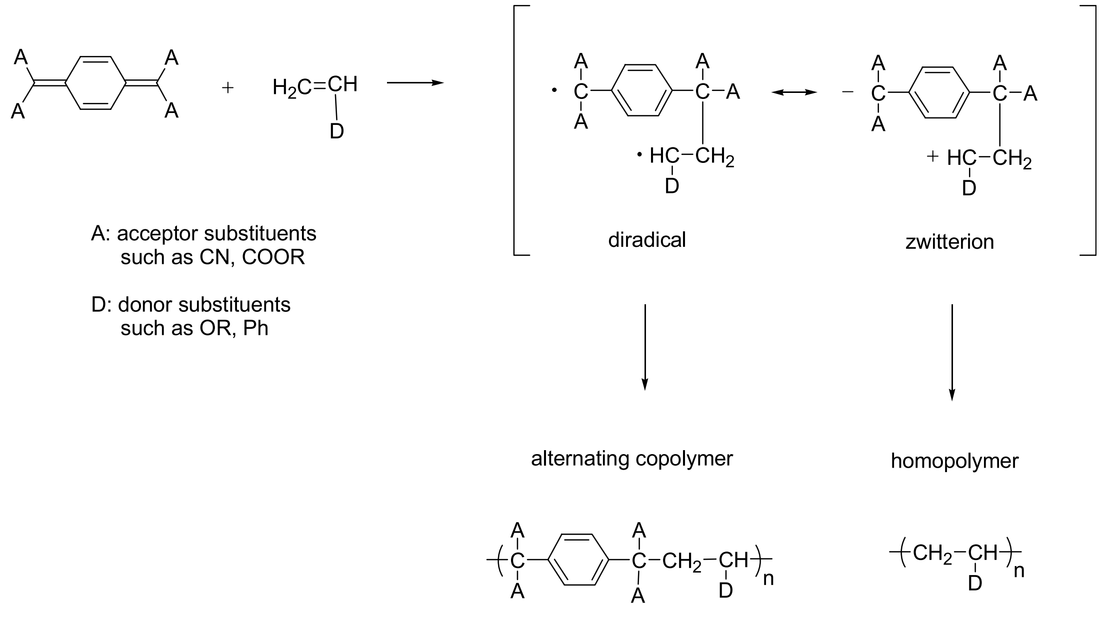
Vinyloxy compounds (*e* value)	Substituted *p*-quinodimethanes (E_1 value, V)[a]				
	2a (−0.83)	**1a** (+0.17)	**4** (+0.20)	**1b** (+0.53)	**1c** (+0.65)
VAc (−0.22)	Al. copoly.	Al. copoly.	Adduct	Al. copoly.	Adduct
PhVE (−1.21)	Al. copoly.	Al. copoly.	Al. copoly.	Al. copoly.	Al. copoly. +homopoly.
CEVE (−1.41)	Al. copoly.	Al. copoly.	Homopoly.	Homopoly.	Homopoly.
BVB (−1.20)	Al. copoly.	Homopoly.	Homopoly.	Homopoly.	Homopoly.
IBVB (−1.77)	Al. copoly.	Homopoly.	Homopoly.	Homopoly.	Homopoly.

Al. copoly., alternating copolymerization; homopoly., homopolymerization.

[a] First reduction potentials (E_1) determined by the cyclovolutammetry in dichloromethane containing $(Bu)_4NClO_4$ using Ag/AgCl as a reference electrode and a platinum wire as a counter electrode.

spontaneous alternating copolymerizations of **1a–c** and **4** with styrene (Table 1), the copolymerization rates all obey the 1.5th-order kinetics with respect to each monomer, although the rate of copolymerization of **1c** with styrene follows the 1st-order kinetics. The 1.5th-order kinetics have been explained well with the mechanism involving the participation of the charge-transfer complex in the initiation and the propagation steps of the copolymerization as shown in Scheme 2 [19,20]. Moreover, these copolymerization rates (defined as the time in a half of acceptor monomer concentration, so-called half-life time) are intimately related to the electron-accepting properties of **1a–c** and **4**, and the rate-determining step has been shown to be the initiation step, where a radical formation by the unimolecular reaction of the charge-transfer complex significantly depends upon the difference in the polar character between both monomers [20]. The copolymerizations of **1a** and **1b** with vinyl monomers having positive *e*-values such as methyl methacrylate (MMA, $e=0.4$), methyl acrylate (MA, $e=0.6$), and acrylonitrile (AN, $e=1.2$) have been investigated in acetonitrile in the presence and absence of AIBN at 60 °C. **1a** copolymerizes alternatingly with MMA in the presence of AIBN. The more electron-accepting **1b** also polymerize alternatingly with MMA in the absence of AIBN and with MA in the presence of AIBN [19–21]. Both of **1a** and **1b** do not copolymerize with AN having a larger positive *e*-value than MMA and MA even in the presence of AIBN. Even vinyl monomers with positive *e*-values, generally classified as the acceptor monomers, may act as donor monomers when they meet the strong electron-accepting substituted *p*-quinodimethanes such as **1a** and **1b**. This behavior cannot been explained by the Alfrey–Prices's scheme in a conventional radical copolymerization, where an alternating tendency is related to the polarity of monomers and expressed as an attractive force between monomers, defined as the $\exp(-e_1 \times e_2)$. Therefore, the attractive force between monomers has been pointed out to be the charge-transfer interaction rather than a Coulomb-type polar interaction.

The spontaneous polymerizations of the electron-accepting substituted *p*-quinodimethanes such as **1a–c**, **2a**,



Scheme 3.

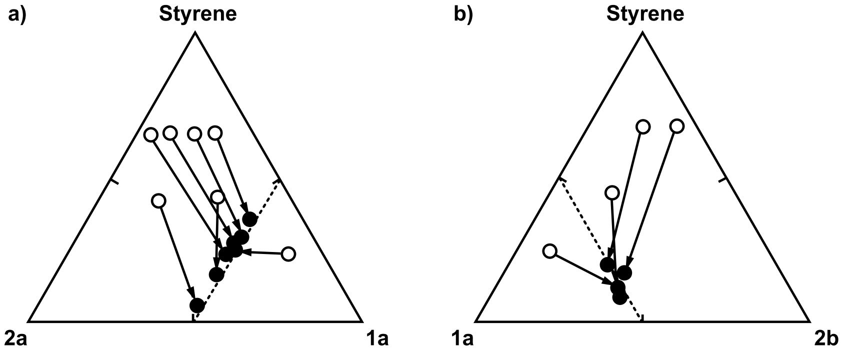
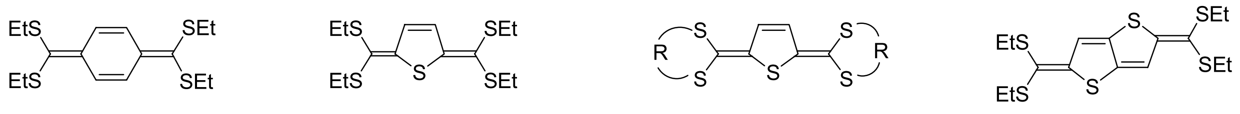


Fig. 1. Triangular diagrams of the composition of (a) the terpolymer of **1a**, **2a**, and styrene and (b) the terpolymer of **1a**, **2b**, and styrene: (○), feed composition; (●), terpolymer composition. Arrows donate change in the composition from the feeds to the terpolymers obtained.

2b, **3**, and **4** with vinyloxy compounds such as butyl vinyl ether (BVE), isobutyl vinyl ether (IBVE), 2-chloroethyl vinyl ether (CEVE), phenyl vinyl ether (PhVE), and vinyl acetate (VAc) takes place in two modes of polymerization (homopolymerization and alternating copolymerization) depending upon a difference in the polarity between these electron-accepting substituted *p*-quinodimethanes and vinyloxy compounds (Table 2). The combination of strong electron-accepting substituted *p*-quinodimethanes with strong electron-donating vinyloxy compounds (monomers with large negative *e*-values) forms a zwitterions intermediate, which initiates cationic polymerizations of vinyloxy compounds. On the other hand, the combination of weak electron-accepting substituted *p*-quinodimethanes with weak electron-donating vinyloxy compounds (monomers with small *e*-values) forms a diradical intermediate via a charge-transfer complex, which induces the alternating copolymerization. Furthermore, in the combination of **1a** with CEVE, an alternating copolymerization takes place in a less polar acetonitrile and the homopolymerization of CEVE proceeds in a higher polar propylene carbonate and in a polar and basic dimethyl sulfoxide (DMSO) and DMF. This solvent effect on the polymerization mode of **1a** with CEVE has been explained well with the polarity and the basicity of the solvents used, that is, with the dependence of the charge transfer complex formation and the electron transfer reaction on the polarity of the solvents and the stabilization of the resulting cationic species by solvation [16,17,19,20,25,26]. The mode of these spontaneous polymerizations might be explained with the bond-forming initiation theory proposed by Hall et al. where the diradical species and zwitterion one lead to alternating copolymer and homopolymer, respectively, as shown in Scheme 3 [2, 27–29]. The concept in the formation of the zwitterion intermediate as a reactive species has been also proposed for the spontaneous reactions of **1a** with alkyl vinyl ethers [30] and with 1-methoxycyclopentene and 1-methoxy- and 1-trimethylsiloxy-1-cyclohexenes [31].

Both of **2a** [17] and 7,7,8,8-tetrakis(ethoxycarbonyl)quinodimethane (**2b**) [32] are weaker electron-accepting substituted *p*-quinodimethanes than **1a**. Both of **2a** and **2b** form the charge-transfer complexes with styrene, and a comparison of the charge-transfer absorption bands has showed that **2a** has a slightly stronger electron-accepting property than **2b**. Both **2a** and **2b** copolymerize alternatingly and spontaneously as acceptor monomers with styrene. Interestingly, both the substituted *p*-quinodimethanes (**2a** and **2b**) form the charge-transfer complexes with a strong electron-accepting **1a**, and also copolymerize alternatingly and spontaneously with it in acetonitrile. A typical acceptor monomer maleic anhydride (electron affinity (EA) = 1.33 eV) [33], which is a weaker electron-accepting monomer than **2b** (EA = 2.27 eV) [33], may form the charge-transfer complex with **1a**, but does not copolymerize alternatingly and spontaneously with **1a**. Therefore, the alternating copolymerization behaviors of **2a** or **2b** with **1a** are related to the highly conjugation (high reactivity) of the substituted *p*-quinodimethanes. The terpolymers formed in the terpolymerizations of styrene, **2a**, and **1a**, and of styrene, **2b**, and **1a** always contain 50 mol% of the **1a** unit regardless of the monomer feed ratios as shown in Fig. 1, which shows truly that **1a** acts as an acceptor monomer, and **2a** or **2b** and styrene do as donor monomers. The amphoteric behavior of **2a** and **2b** in the alternating copolymerizations depending upon the comonomer has been explained well by a relative difference in the π-electron density among styrene, **2a** and **2b**, and **1b**, where the styrene has the highest π-electron density followed by **2a** and **2b**, and **2a** has the lowest π-electron density (a proposal of π-electron density scheme) [17]. This is the first example of the amphoteric behavior of the substituted *p*-quinodimethanes doing an alternating copolymerization.

Terpolymerizations in a combination of two alternating copolymerization systems such as the two acceptor monomers and a common donor monomer, and two donor monomers and a common acceptor monomer provide a suitable method to determine the relative reactivities of two acceptor monomers and of two donor monomers. From the application of this method to the terpolymerization



7

8a

8 b: R= CH_2CH_2
c: R= $CH(CH_3)CH(CH_3)$
d: R= $CH_2CH_2CH_2$

9

Chart 2.

composed of the two alternating copolymerization systems of **5a** with styrene and of **5b** with styrene, **5b** has been found to be more reactive as an acceptor monomer than **5a**, and, moreover, the higher reactivity of **5a** compared to **5b** is supported from the addition reaction rates with AIBN [22]. The relative reactivity can be explained well by the energy difference between the quinonoid structure and the benzenoid structure for **5a** and **5b**.

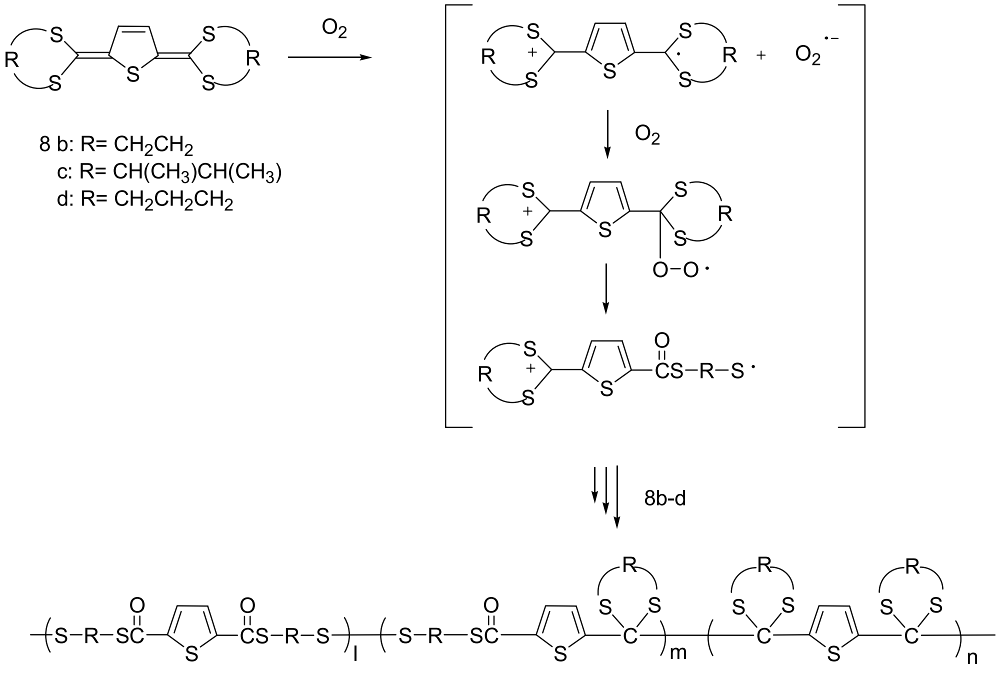
2.2. Electron-donating substituted p-quinodimethanes with same substituents

The following electron-donating substituted *p*-quinodimethanes, 7,7,8,8-tetrakis(ethylthio)quinodimethane (**7**) [34], and its thiophene and thieno[3,2-b]thiophene analogues, 2,5-bis[(diethylthio)methylene]-2,5-dihydrofuran (**8a**) [23], 2,5-bis(1′,3′-dithiolan-2′-ylidene)-2,5-dihydrothiophene (**8b**) [35], 2,5-bis(4′,5′-dimethyl-1′,3′-dithiolan-2′-ylidene)-2,5-dihydrothiophene (**8c**) [35], 2,5-bis(1′,3′-dithian-2′-ylidene)-2,5-dihydrothiophene (**8d**) [36], and 2,5-bis[(diethylthio)-methylene]-2,5-dihydrothieno[3,2-b]thiophene (**9**) [24] as shown in Chart 2 have been synthesized.

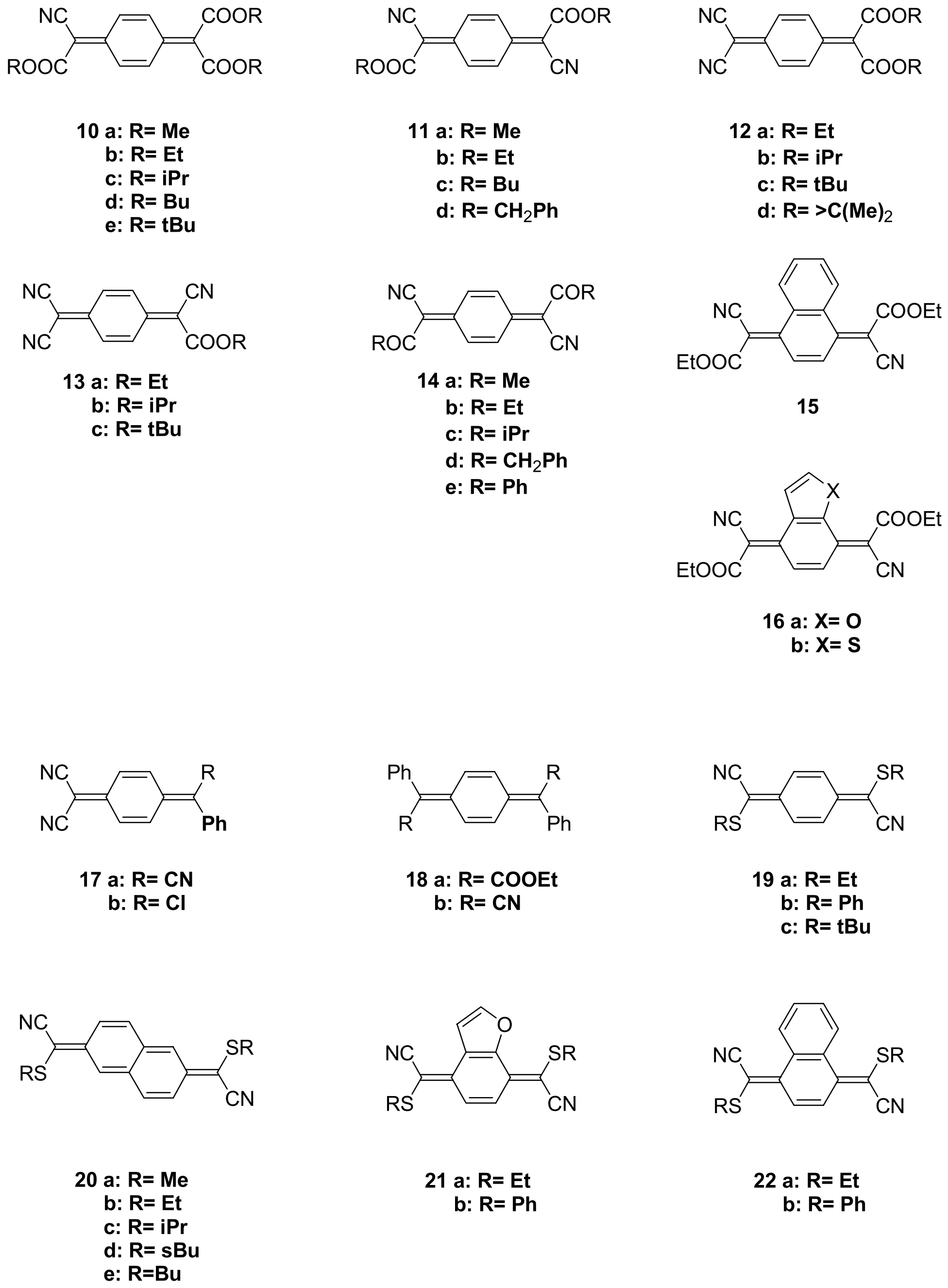
Electron-donating substituted *p*-quinodimethane and thiophene and thieno[3,2-b]thiophene analogues (**7**, **8a**, and **9**) except for **8b–d** are not homopolymerizable with any initiators. From the reaction product analysis with an excess amount of initiator, it has been found that no polymerizations are due to a lack of propagation for the radical and cationic initiators and a lack of initiation for the anionic initiator, respectively [23,24]. **8b–d** with heterocyclic rings polymerize spontaneously in the presence of oxygen to give polymers composed of three structural units containing a thioester group formed by ring-opening reactions of dithiolan and dithian rings with oxygen and the ratios of the structural units are dependent upon a polarity of solvents used and polymerization conditions [35,36]. A plausible polymerization mechanism via a radical-cation intermediate as shown in Scheme 4 has been proposed.

2.3. Electron-accepting substituted p-quinodimethanes with different substituents

Electron-accepting substituted *p*-quinodimethanes with different substituents at 7 and 8 positions as shown in



Scheme 4.



10 a: R= Me
b: R= Et
c: R= iPr
d: R= Bu
e: R= tBu

11 a: R= Me
b: R= Et
c: R= Bu
d: R= CH_2Ph

12 a: R= Et
b: R= iPr
c: R= tBu
d: R= $>C(Me)_2$

13 a: R= Et
b: R= iPr
c: R= tBu

14 a: R= Me
b: R= Et
c: R= iPr
d: R= CH_2Ph
e: R= Ph

15

16 a: X= O
b: X= S

17 a: R= CN
b: R= Cl

18 a: R= COOEt
b: R= CN

19 a: R= Et
b: R= Ph
c: R= tBu

20 a: R= Me
b: R= Et
c: R= iPr
d: R= sBu
e: R=Bu

21 a: R= Et
b: R= Ph

22 a: R= Et
b: R= Ph

Chart 3.

Chart 3 have been synthesized and they are isolable as crystals in a monomeric state. As substituted *p*-quinodimethanes carrying two different electron-accepting substituents, cyano, alkoxycarbonyl, and acyl groups, there are a number of species, including 7,7,8-tris(alkoxycarbonyl)-8-cyano-*p*-quinodimethanes (**10a**–**e**) [37], 7,8-bis(alkoxycarbonyl)-7,8-dicyano-*p*-quinodimethanes (**11a**–**d**) [38–42], 7,7-bis(alkoxycarbonyl)-8,8-dicyano-*p*-quinodimethanes (**12a**–**d**) [43], 7-alkoxycarbonyl-7,8,8-tricyano-*p*-quinodimethanes (**13a**–**c**) [43], 7,8-diacyl-7,8-dicyano-*p*-quinodimethanes (**14a**–**e**) [44,45], 11,12-bis(ethoxycarbonyl)-11,12-dicyano-1,4-naphthoquinodimethane (**15**) [46], 4,7-bis[(ethoxycarbonyl)cyanomethylene]-4,7-dihydrobenzofuran (**16a**) [46], 4,7-bis[(ethoxycarbonyl)cyanomethylene]-4,7-dihydrobenzothiophene (**16b**) [46], and the substituted *p*-quinodimethanes carrying both electron-accepting substituents such as cyano and ethoxycarbonyl groups and electron-donating substituents such as alkylthio and phenyl groups, include 7,7,8-tricyano-8-phenyl-*p*-quinodimethane (**17a**) [47], 7,7-dicyano-8-chloro-8-phenyl-*p*-quinodimethane (**17b**) [48], 7,8-bis(ethoxycarbonyl)-7,8-diphenyl-*p*-quinodimethane (**18a**) [49], 7,8-dicyano-7,8-diphenyl-*p*-quinodimethane (**18b**) [50,51], 7,8-bis(alkylthio)-7,8-dicyano-*p*-quinodimethanes (**19a**–**c**) [52,53],

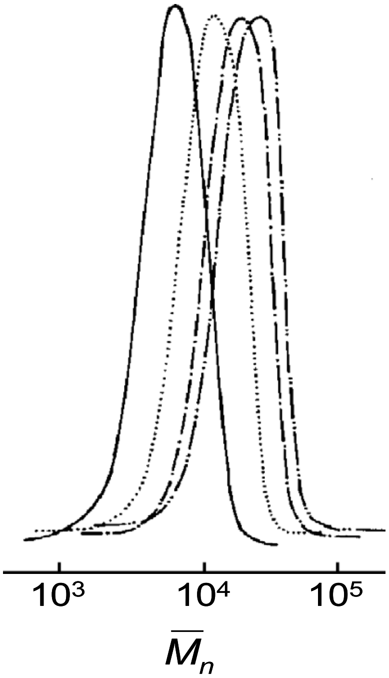


Fig. 2. GPC curves of poly(**16a**) with three monomer solution additions. Initiator, butyllithium; polymerization temperature, 0 °C; solvent, THF; monomer concentration, 10.7 mmol/L; volume of the monomer solution at each addition, 15 mL. (1) The initial polymerization at [**16a**]/[BuLi] = 13.9; (—), M_n of the polymer = 5,600 and polydispersity (M_w/M_n) = 1.22. (2) After the first monomer solution addition; (- - -), M_n = 11,000 and M_w/M_n = 1.20. (3) After the second addition; (- · -), M_n = 17,000 and M_w/M_n = 1.20. (4) After the third addition; (- · · -), M_n = 24,000 and M_w/M_n = 1.20.

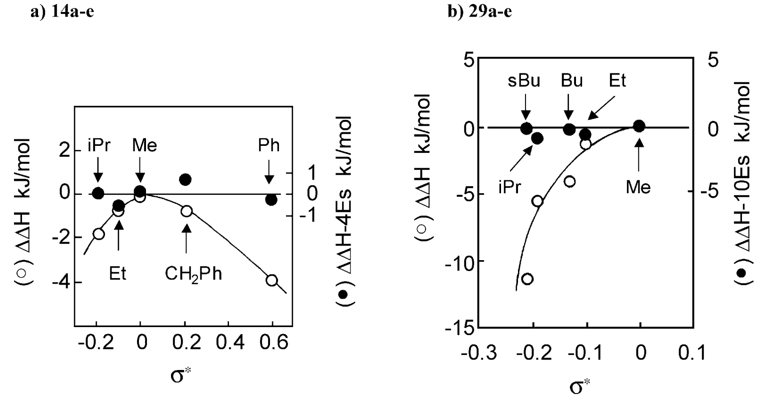
11,12-bis(alkylthio)-11,12-dicyano-2,6-naphthoquinodimethanes (**20a**–**e**) [54], 4,7-bis[(alkylthio)cyanomethylene]-4,7-dihydrobenzofurans (**21a**,**b**) [55], and 11,12-bis(alkylthio)-11,12-dicyano-1,4-naphthoquinodimethanes (**22a**,**b**) [55].

The homopolymerizabilities of these substituted *p*-quinodimethanes and their copolymerization behaviors with styrene significantly depend upon the type, number, combination, and size of the substituents at the exocyclic positions. The nature of the aromatic rings is also important. The substituted *p*-quinodimethanes based on naphthalene, benzofuran, and benzothiophene rings such as **15**, **16a**,**b**, **21a**,**b**, and **22a**,**b** and variants with phenyl groups at the exocyclic positions such as **17a**,**b** and **18a**,**b** do not homopolymerize with any initiators, but other substituted *p*-quinodimethanes (**10a**–**e**, **11a**–**d**, **12a**–**d**, **13a**–**c**, and **14a**–**e**) homopolymerize with a radical initiator such as AIBN, an anionic initiator such as butyllithium, and a weak base such as triethylamine and pyridine. **19a** polymerizes with all type of initiators such as free radical, anionic, and cationic initiators like as styrene and 1,3-butadiene. This is attributable to the strong resonance stabilization by the captodative effect [56] and to the neutral polarity. And also, when these homopolymerizable substituted *p*-quinodimethanes have been dissolved in the polar basic solvents (tetrahydrofuran (THF), DMF, DMSO, acetonitrile, and acetone), their homopolymerizations take place to give corresponding oligomers or polymers with high molecular weight, but do not on dissolving them in the non-basic solvents (chloroform, dichloromethane, toluene, and benzene) [39,44,52]. The polymerizations observed in the polar basic solvents are considered to proceed through an anionic mechanism. The anionic homopolymerizations of **11c** in toluene and of **16a** in THF with a butyllithium initiator at 0 °C have been investigated [39,46]. Both anioic polymerizations proceeds in a living-like manner. The monomer addition experiments for the polymerization of **16a** initiated by a butyllithium initiator are shown in Fig. 2. After each monomer addition, the peak position in the gel permeation chromatography (GPC) charts moves to higher molecular weight sides with keeping a sharp unimodal shape, indicating that the polymeric species produced after the monomer has completely been consumed is still able to react with added monomer molecules (**16a**) and to grow to a polymeric species with a higher molecular weight. Similar behavior has been observed in the polymerization of **11c**.

As to the radical homopolymerizations for the homopolymerizable substituted *p*-quinodimethanes (**11c**, **14a**–**e**, **16a**, and **19a**,**b**), from their detailed kinetic studies, these polymerizations have been found to be a typical equilibrium polymerization involving a considerable degree of depolymerization. On the basis of the equilibrium polymerization behavior, thermodynamic parameters, enthalpy and entropy changes of polymerization, for the substituted *p*-quinodimethanes (**11**, **14a**–**e**, and **19a**,**b**) are determined and

Table 3
Equilibrium monomer concentration ($[M]_e$) and enthalpy change (ΔH) and entropy change (ΔS) of polymerizations

Temp. (°C)	($[M]_e$)×10^3, (mol/L)									
	11c	**14a**	**14b**	**14c**	**14d**	**14e**	**19a**	**19b**	Styrene	α-Me-styrene
40		4.98	7.05	13.2		23.6	6.59	6.97		
50	4.46	6.51	9.4	17.5	4.8	29.5	8.40	8.51		
60	6.50	9.17	12.4	22.7	6.4	36.6	11.5	12.1		
70	7.91	11.2			8.2	47.6				
$-\Delta H$ (kJ/mol)	26.4	25.4	24.5	23.5	24.6	21.6	24.1	24.6	73	35
$-\Delta S$ (J/K mol)	36.9	36.8	37.0	39.1	37.0	37.5	35.1	37.0	104	100

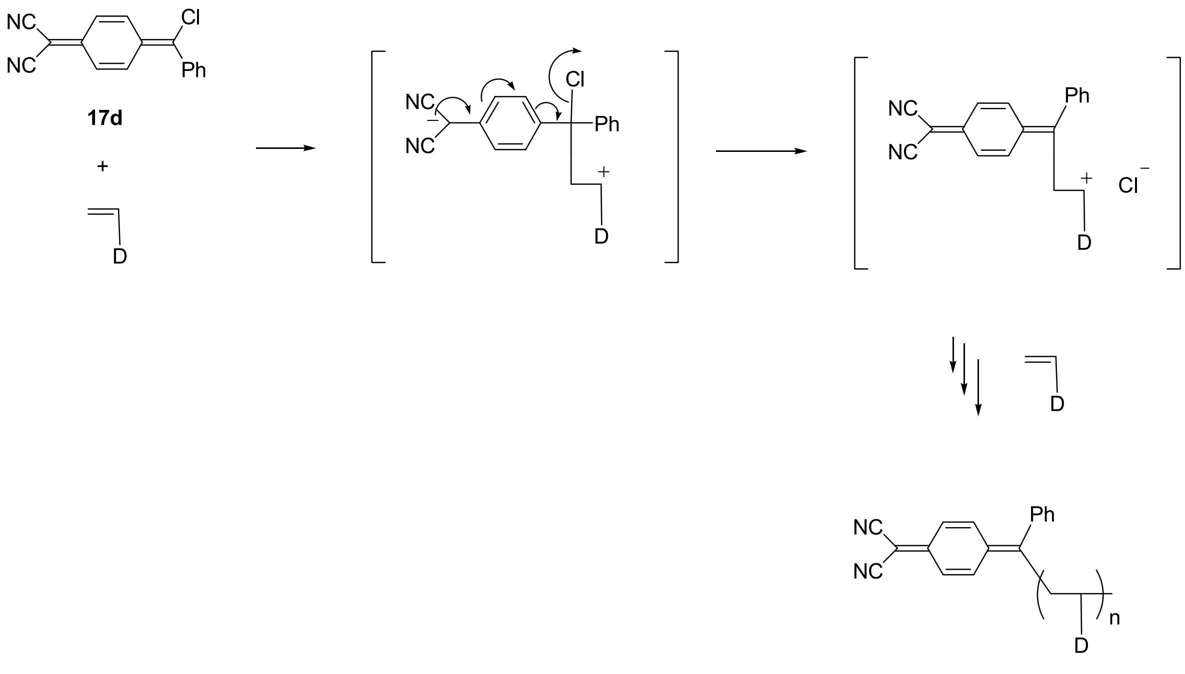

a) 14a-e

b) 29a-e

Fig. 3. The plots of (a) $\Delta\Delta H$ vs σ^* (○) and $\Delta\Delta H-4$Es vs σ^* (●) for the polymerizations of the **14a–e** and (b) $\Delta\Delta H$ vs σ^* (○) and $\Delta\Delta H-10$Es vs σ^* (●) for the polymerizations of the **20a–e**.

summarized in Table 3 together with the equilibrium monomer concentrations.

The enthalpy (ΔH) changes of polymerization vary with the substituents in the range of 20–30 kJ/mol though the values are small, and the entropy (ΔS) changes are regarded as almost constant as about 40 J/K mol, which is about 1/3 as large as the corresponding values (100–130 J/K mol) for vinyl and related monomers. Both of ΔH and ΔS values are relatively small, but a combination of two values give a negative free energy value for the polymerization of these substituted *p*-quinodimethanes, and, therefore, the polymerizations can proceed. Small values of ΔH and ΔS are one of unique features for the polymerizations for the substituted *p*-quinodimethanes. The substituent effect on the polymerizability of the substituted *p*-quinodimethanes has been investigated by analyzing the thermodynamic parameters with a linear free energy relationship. The analyses of the enthalpy changes for the polymerizations of **14a–e** and of **20a–e** with the Taft equation ($\Delta H=\rho^*\sigma^*+\delta$Es) using polar substituent constants, σ^*, and steric substituent constants, Es, of the alkyl groups on the substituents are shown in Fig. 3. The plots of $\Delta\Delta H$ with σ^* for both systems have been found to be convex. The plots of $\Delta\Delta H-4$Es for **14a–e** and of $\Delta\Delta H-10$Es for **20a–e**, where the steric hindrance is taken into account, give straight lines with slops of zero, $\rho^*=0$. This indicates that the ΔH depends only on the steric hindrance of the acyl or alkylthio substituents, but not on the polar effect of them. It has been concluded, therefore, that the homopolymerizability of the substituted *p*-quinodimethanes is determined exclusively by a steric hindrance effect arising from the substituents at the exocyclic positions [45,54]. The reason why the substituted *p*-quinodimethanes with bulky *tert*-butyl substituents such as **12d**, **13c**, and **19c** becomes isolable crystals at room temperature and are not or



Scheme 5.

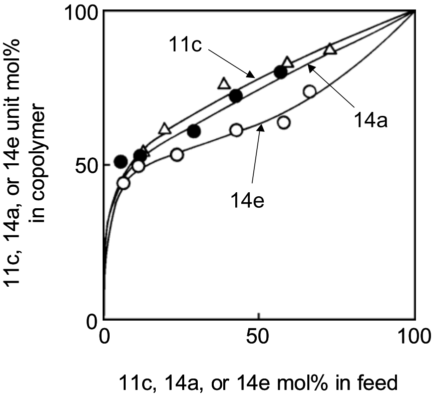


Fig. 4. Copolymerization composition diagrams for the **11c**-styrene (△), **14a**-styrene (●), and **14e**-styrene (○) systems at 50 °C.

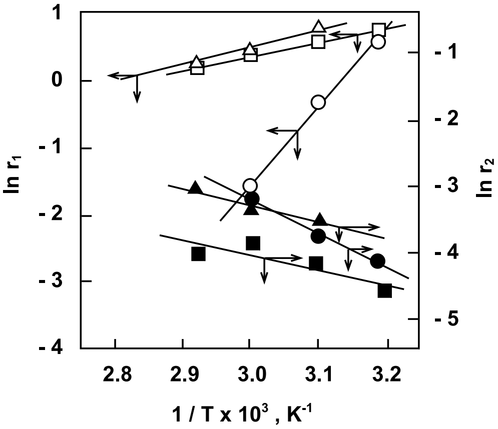


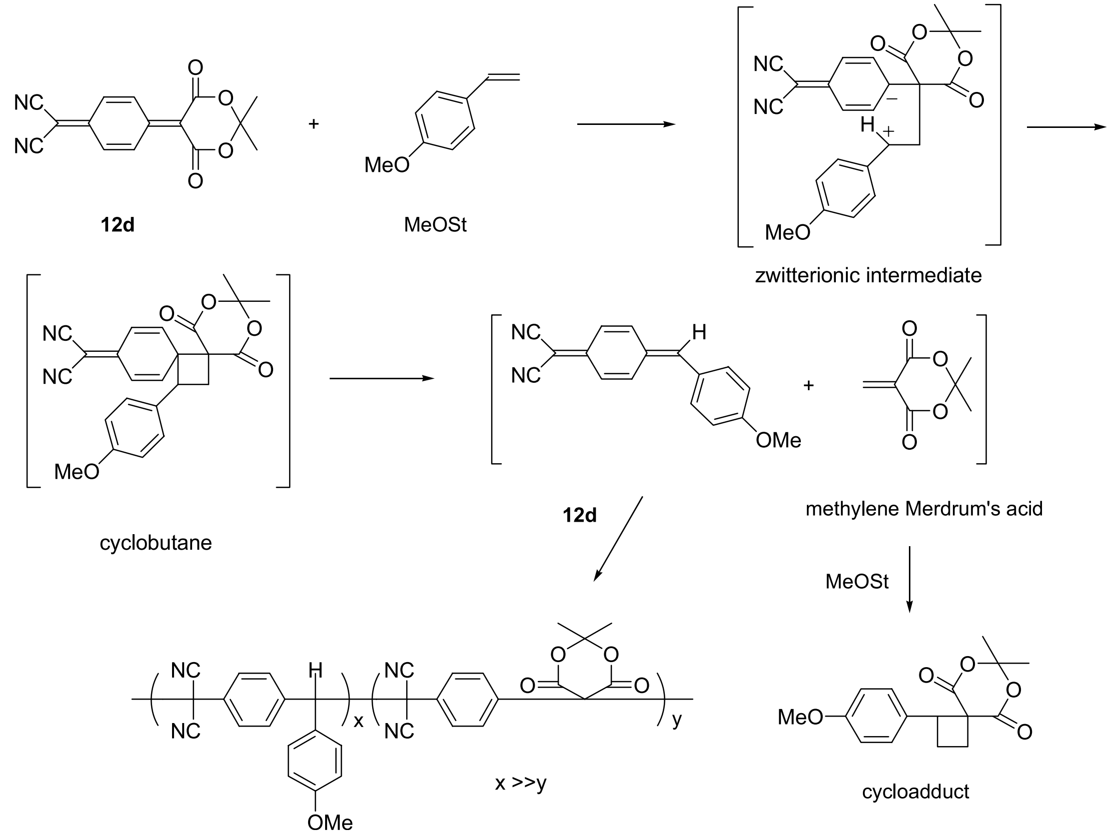
Fig. 5. The relationships of logarithms of monomer reactivity ratios ln r_1 and ln r_2 vs reciprocal absolute temperature $1/T$ for the **14e**-styrene (r_1(○), r_2(●)), **14a**-styrene (r_1(□), r_2(■)), **11c**-styrene (r_1(△), r_2(▲)) systems.

hardly homopolymerizable is probably attributable to this steric hindrance effect. **17b** acts as an initiator for cationic homopolymerizations of *p*-methoxystyrene, isobutyl vinyl ether, *N*-vinylcarbazole, and 1,3-dioxepane, where a chloride anion formed by an elimination reaction from a phenylene-tetramthylene zwitterion intermediate is a counter ion as shown in Scheme 5 [48].

Among all substituted *p*-quinodimethanes in the Chart 3, non- or hardly-homopolymerizable substituted *p*-quinodimethanes such as **10e**, **15**, **16a**,**b**, **17a**, **18a**,**b**, **21a**,**b**, and **22a**,**b** copolymerize with styrene in the presence of AIBN in an alternating fashion, while the homopolymerizable *p*-quinodimethanes such as **10a–d**, **11a–d**, **14a–e**, and **19a**,**b** do with styrene in a random fashion. As shown in Fig. 4, **11c**, **14a**, and **14e** copolymerize with styrene in a random fashion at the monomer concentration higher than the respective equilibrium monomer concentrations, and the copolymerizations can be analyzed without a deviation by the Kelen–Tüdös method proposed for the conventional radical polymerization, that is, for the terminal model of the copolymerization. The monomer reactivity ratios at the different temperatures in these copolymerization systems are listed in Table 4 and the relationship of the monomer reactivity ratios with reciprocal absolute polymerization temperatures is shown in Fig. 5 [57]. The monomer reactivity ratios approach to unity with an increase in a polymerization temperature in the conventional radical copolymerization, that is, becoming an ideal copolymerization, However, in the copolymerizations of the substituted *p*-quinodimethanes with styrene, the monomer reactivity ratios approach to zero, not to unity with an increase in the temperatures as indicated with the temperature dependence of the r_1 value in the copolymerization of the **14e**-styrene system, that is, this copolymerization approaches not to an ideal copolymerization type but to an alternating one. Moreover, the change in the copolymerization mode is significant for the **14e**-styrene system with a larger degree of the depolymerization compared to the **11c**-styrene and **14a**-styrene systems, indicating that the copolymerization modes are intimately related to the equilibrium polymerizabilities of these substituted *p*-quinodimethanes. To look into the effect of equilibrium polymerization of **11c** and **14e** on the kind of polymerization, copolymerizations of **11c** and **14e** with *p*-substituted styrenes have been carried out under same polymerization conditions considering their equilibrium monomer concentrations, and the cross-propagation steps, especially the addition step of the polymer radical with a terminal substituted *p*-quinodimethane unit to *p*-substituted styrenes, are analyzed by a linear free energy relationship [58]. The cross-propagation steps become largely controlled by a polar effect rather than a resonance (general reactivity) with an increase in the degree of the depolymerization. On the basis of these findings, we have proposed a new concept for the radical alternating

Table 4
Monomer reactivity ratios of the copolymerizations for the **11c**-styrene, **14a**-styrene, and **14e**-styrene systems

System		Monomer reactivity ratios (r_1 and r_2)			
		40 (°C)	50 (°C)	60 (°C)	70 (°C)
14e-Styrene	r_1	1.78±0.32	0.73±0.2	0.16±0.12	
	r_2	0.025±0.01	0.021±0.015	0.026±0.01	
14a-Styrene	r_1	2.06±0.32	2.02±0.2	1.46±0.24	1.12±0.32
	r_2	0.017±0.014	0.015±0.01	0.021±0.012	0.023±0.02
11c-Styrene	r_1		2.59±0.2	1.49±0.16	1.21±0.22
	r_2		0.03±0.01	0.033±0.017	0.05±0.015

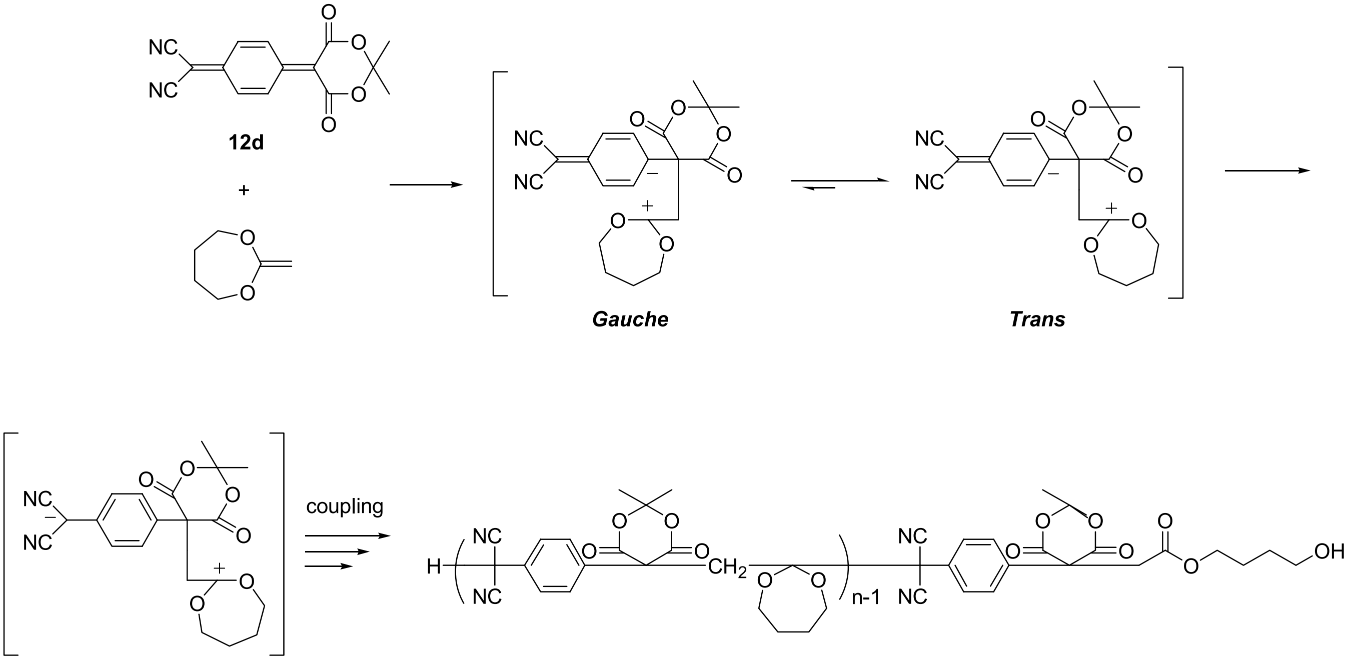


Scheme 6.

copolymerization mechanism [33,38]. In the copolymerization system of electron-accepting substituted *p*-quinodimethane with styrene, electron-accepting substituted *p*-quinodimethane is much more conjugative (reactive) than styrene. Therefore, the polymer radical with the terminal styrene unit reacts almost exclusively with electron-accepting substituted *p*-quinodimethane. Then, the resulting polymer radical with the terminal electron-accepting substituted *p*-quinodimethane reacts with either electron-accepting substituted *p*-quinodimethane or styrene when the monomer concentration of electron-accepting substituted *p*-quinodimethane is higher than its equilibrium concentration, leading to a random copolymerization. When the monomer concentration of the electron-accepting substituted *p*-quinodimethane is lower than its equilibrium monomer concentration, the addition reaction of the resulting polymer radical with the terminal electron-accepting substituted *p*-quinodimethane unit to the electron-accepting substituted *p*-quinodimethane monomer does not occur because of the depolymerization. The addition reaction of the resulting polymer radical with the terminal electron-accepting substituted *p*-quinodimethane unit to the styrene monomer is the slowest reaction because the most conjugative (least reactive) polymer radical reacts with the least conjugative (least reactive) monomer, corresponding to the most disadvantage reaction in view of reaction energy theory. However, the resulting polymer radical with the terminal electron-accepting substituted *p*-quinodimethane unit could undergo a cross-propagation reaction in favor of a strong charge-transfer interaction with styrene monomer due to the great difference in the polarity between the two reacting species, leading to an alternating copolymerization.

10e is not homopolymerizable with a radical initiator because of the existence of a bulky *tert*-butoxy group, but copolymerizable with styrene and also with **1a** like **2a**,**b**. This is one more example, which exhibits an amphoteric behavior in both the charge-transfer complex formation and the alternating copolymerization [37].

The spontaneous copolymerizations of substituted *p*-quinodimethanes like **11b**, **17a** and **12d** with donor monomers such as styrene, *p*-methoxystyrene (MeOSt), *N*-vinylcarbazole, isobutyl vinyl ether, and 2-chloroethyl vinyl ether have been explained well with a bond-forming initiation mechanism, where a zwitterionic phenylene-tetramethylene intermediate or a diradical one is formed as an initiating species. For the spontaneous alternating copolymerizations for the **11b**-styrene and **17a**-styrene systems, the diradical phenylene-tetramethylene intermediate is to be an initiating species leading to the alternating copolymers [50,51]. In the spontaneous reaction of **12d** with MeOSt [59], the mechanism as shown in Scheme 6, where the trisubstituted *p*-quinodimethane and a methylene



Scheme 7.

Meldrum's acid are formed by the methathesis reaction via the zwitterionic tetramethylene intermediate, and the former copolymerizes with **12d** via a radical mechanism and the latter reacts with MeOSt to form a 1:1 cycloadduct of methylene Meldrum's acid:MeOSt, has been proposed.

On the other hand, in the spontaneous reaction of **12d** with cyclic ketene acetal 2-methylene-1,3-dioxepane, the trans-form zwitterionic tetramethylene intermediate is formed as an initiating species by a steric repulsion between the quinonoid ring of **12d** and the bulky cyclic 1,3-dioxepane ring, and then it is transformed to a zwitterionic phenylene-tetramethylene intermediate, which gives an alternating copolymer via its coupling reaction (Scheme 7) [60]. The bond-forming initiation theory [27,29] proposed for the spontaneous reactions of the electron deficient olefins and electron rich olefins have been shown to be applicable to the spontaneous polymerizations of the substituted *p*-quinodimethanes with donor monomers.

2.4. Electron-accepting and electron-donating substituted p-quinone methides

The following substituted *p*-quinone methides, 7-phenyl-2,6-dimethyl-*p*-quinone methides (**23a–d**) [61], 7-[1′-(*o*-methoxy)phenoxyethyl]-2-methoxy-*p*-quinone methide (**24**) [62], 7,7-bis(trifluoromethyl)-*p*-quinone methides (**25a–d**) [63,64], 7,7-dicyano-*p*-quinone methides (**26a**,**b**) [65,66], 7-alkoxycarbonyl-7-cyano-*p*-quinone methides (**27a–f**) [67,68], 7,7-bis(alkoxycarbonyl)-*p*-quinone methides (**28a–c**) [69], and 7-cyano-7-phenyl-*p*-quinone methide (**29**) [70] have been synthesized (Chart 4).

The electron-donating substituted *p*-quinone methides **23a–d** polymerize with potassium *tert*-butoxide in THF to give high molecular weight polymers which can be cast into clear films. Their polymerization rates are significantly affected by the *para*-substituent on the 7-phenyl ring of **23a–d**. A large enhancement in the rates have been observed

Table 5
Asymmetric anionic polymerization of **23b** with various chiral anionic initiators

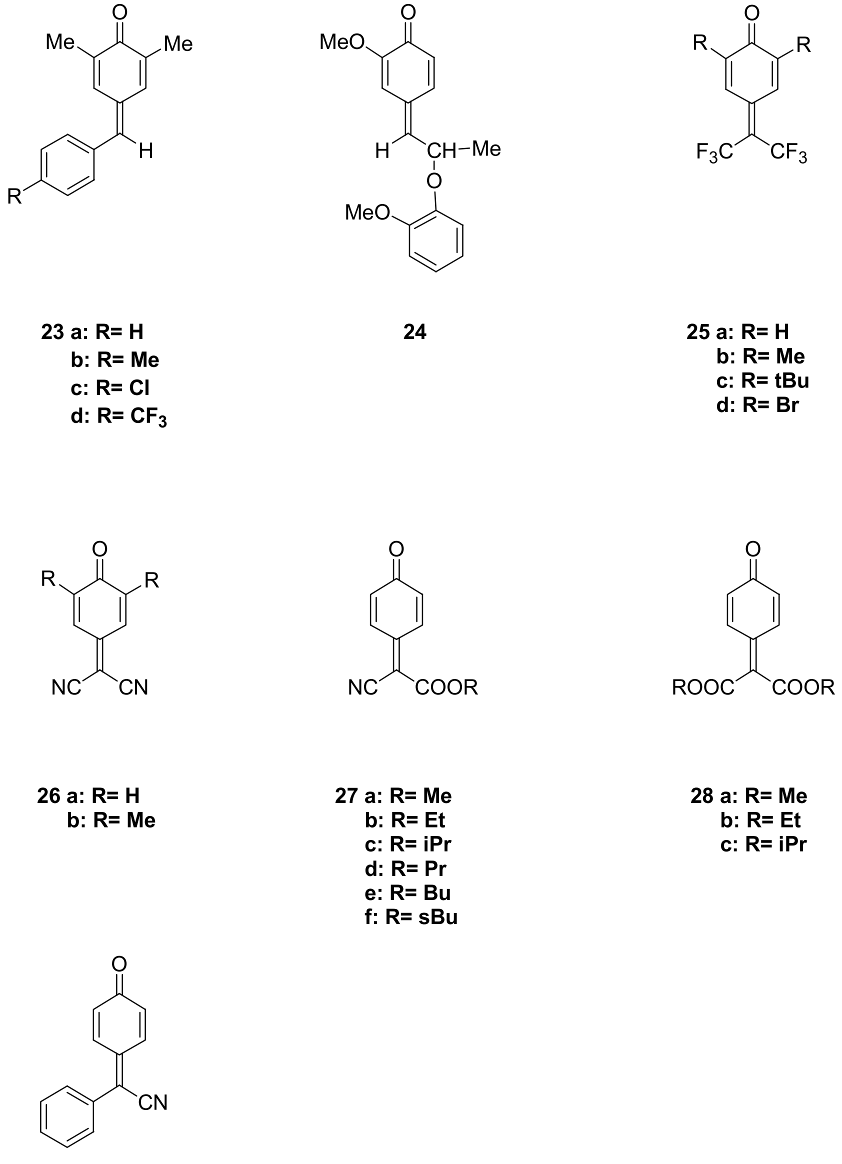
Entry	Initiator	Ligand	Time (h)	Yield[a] (%)	M_n[b]	M_w/M_n[b]	$[\alpha]_{435}$[c](°)
1	*n*-BuLi	(−)-Sp	24	79	4700	1.14	−9.1
2	*i*-PrPhOLi	(−)-Sp	72	59	4300	1.31	−22.5
3	FlLi	(−)-Sp	24	63	3400	1.67	−26.8
4	FlLi	(+)-MMP	24	47	1700	1.53	−3.8
5	FlLi	(+)-PMP	24	36	2900	1.39	+4.5
6	FlLi	(+)-DDB	24	76	4400	1.48	−6.6

[**23b**] = 0.48 mol/L, [**23b**]/[initiator] = 20; temp., 0 °C.

[a] Methanol-insoluble part.

[b] Determined by GPC (polystyrene standards).

[c] In chloroform.



23 a: R= H
b: R= Me
c: R= Cl
d: R= CF_3

24

25 a: R= H
b: R= Me
c: R= tBu
d: R= Br

26 a: R= H
b: R= Me

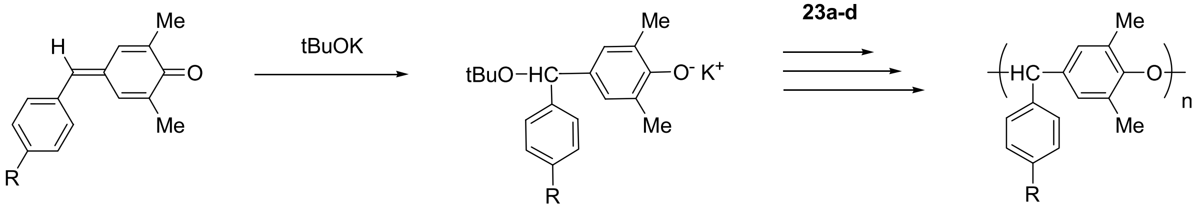
27 a: R= Me
b: R= Et
c: R= iPr
d: R= Pr
e: R= Bu
f: R= sBu

28 a: R= Me
b: R= Et
c: R= iPr

29

Chart 4.

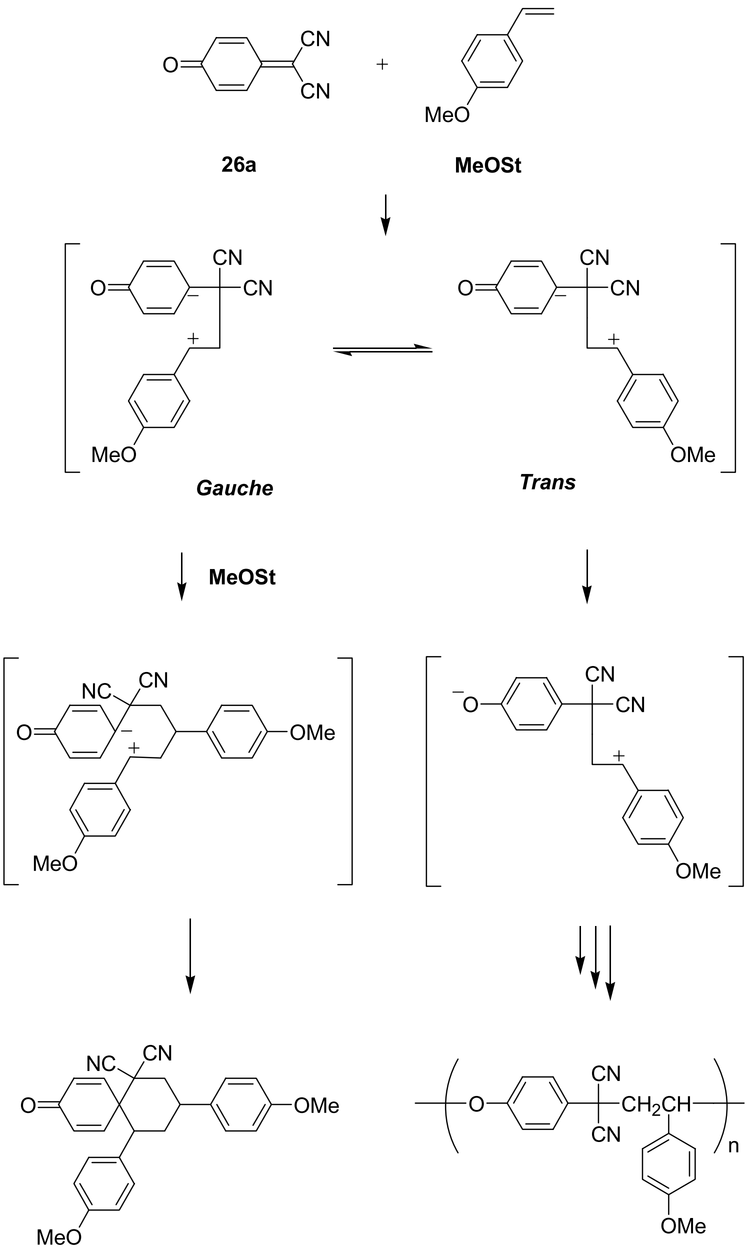
for more electron-withdrawing groups. This supports the anionic mechanism as shown in Scheme 8, where the *tert*-butoxide anion attacks the exocyclic carbon site of **23a–d** to form a more stable phenolate anion, followed by subsequent additions to give a polymer with head-to-tail placements [61]. Asymmetric anionic polymerizations of **23a** with chiral anionic initiators such as complexes of fluorenyllithium (FlLi) with (−)-sparteine ((−)-Sp),



(R= H, Me, Cl, CF_3)

23a-d

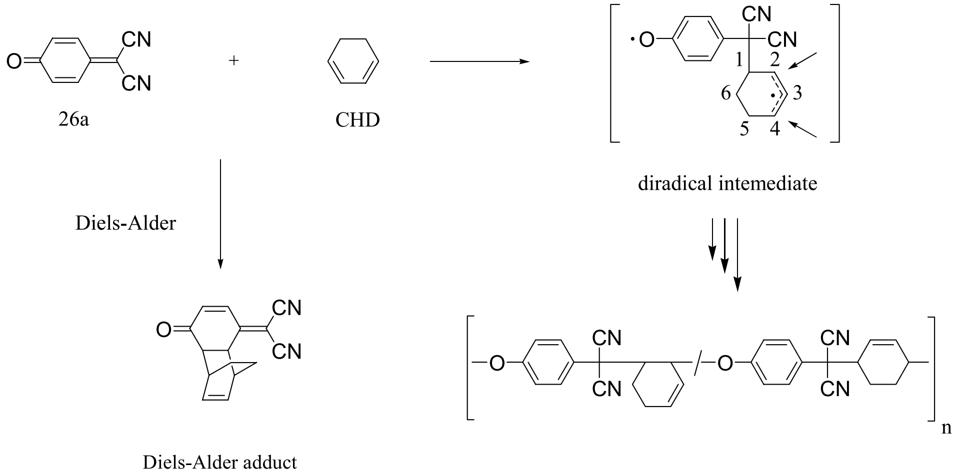
Scheme 8.



Scheme 9.

(*R*)-(+)-2-(methoxymethyl)pyrrolidine ((+)-MMP), (*S*)-(+)-1-(2-pyrrolidinylmethyl)pyrrolidine ((+)-PMP), (*S*,*S*)-(+)-2,3-dimethoxy-1,4-bis(dimethylamino)butane ((+)-DDB)), of butyllithium with (−)-Sp, and of isopropylphenoxy lithium with (−)-Sp provide optically active polymers with configurational chirality (Table 5). The poly(**23a**) with the largest specific rotation is obtained with a complex of FlLi and (−)-Sp. On the basis of the effects of the initiator concentration and solvent polarity on the specific rotation of the poly(**23a**), the specific rotations have been found to be mainly governed with the aggregation state of the propagating chain end [71]. The polymerization of **24** in acetonitrile and DMF by chemical initiation using tetra-*n*-butylammonium hydroxide, sodium hydroxide, and lithium hydroxide or by electrochemical initiation using tetra-*n*-butylammonium perchlorate and tetraethylammonium perchlorate gives lignin-model polymers. In this polymerization, the nature of the counter cation during the polymerization affects the stereochemistry of the polymers. The erythro isomer is preferencially formed for tetraalkylammonium cations and the threo isomer is for alkali metal cations, respectively [62].

The electron-accepting substituted *p*-quinone methides **25a–d** polymerize anionically with sodium iodide or tetraethylammonium chloride in acetone or with sodium hydroxide or potassium *tert*-butoxide to give crystalline white polymers, which can be pressed into brittle films at 200 °C [63,64]. **26a**, **27a–f**, **28a–c**, and **29** are also



Scheme 10.

homopolymerizable with an anionic initiator such as butyllithium to give the corresponding polymers with a head-to-tail placement like **23a–d** and **24**, but all of these are not homopolymerizable with cationic initiators. **26a**,**b**, **28c**, and **29** are not homopolymerizable with radical initiators, but **28a–d** and **28a**,**b** are homopolymerizable under same polymerization conditions. **27a–f** exhibit a typical equilibrium polymerization behavior like the homopolymerizable *p*-quinodimethanes with the different substituents at 7 and 8 positions mentioned in the Section 2.3. Moreover, the homopolymerizability of the substituted *p*-quinone methides is also determined exclusively by a steric hindrance effect of the alkoxy groups at the exocyclic positions like as the case of the substituted *p*-quinodimethanes. This is based on the analysis of the enthalpy changes of polymerization with a linear free energy relationship [68]. Non-homopolymerizable **28c**, **26a**,**b** and **29** copolymerize alternatingly with styrene, *p*-methoxystyrene, or α-acetoxystyrene to furnish the corresponding alternating copolymers [60,70]. The copolymers of **26a**,**b** with α-acetoxystyrene provides amorphous, transparent, and tough films by solvent-casting methods [66]. The spontaneous reaction mechanism of **26a** with MeOSt leading to an alternating copolymer and a cycloadduct involves a zwitterionic tetramethylene intermediate formation in the initiation step and their coupling reaction in the propagation step as shown in Scheme 9, in which the cycloadduct is formed from the gauche-form zwitterionic tetramethylene intermediate and the alternating copolymer is formed from the zwitterionic phenylene-oxytrimethylene intermediate via a *trans*-form zwitterionic tetramethylene intermediate [72]. On the other hand, the use of cyclohexadiene (CHD) as a donor monomer instead of MeOSt provides both an alternating copolymer with two different structural units of the CHD and a Diels–Alder adduct contrary to the case of MeOSt. The polymerization mechanism involving a diradical phenylene-oxytrimethylene intermediate formation in the initiation step and their coupling reaction in the propagation step as shown in Scheme 10 have been proposed [73]. The spontaneous reaction of **29** with styrene also gives alternating copolymers by the mechanism involving a diradical phenylene–oxytrimethylene intermediate in the initiation step and a chain addition like a conventional radical copolymerization [70].

3. Solid-state polymerizations of electron-accepting substituted *p*-quinonoid monomers

Polymerization is usually carried out in a fluid state such as solution, emulsion, suspension, gas or melt because of easy operation and control of the polymerization conditions which afford an advantage for the production of commercial polymers and polymeric materials. Despite of its wide applicability, however, the polymers obtained are either amorphous or semicrystalline because of the nature of the state. Generally, it is very difficult to obtain macroscopically ordered polymer single crystals by recrystallization of such amorphous or semicrystalline polymers from its solution or melt though the growth of microscopic single crystals may be possible in specific cases. In contrast, polymerization in a solid state may produce unique chain structures and macroscopic polymer single crystals though multi conditions for successful polymerization in solid states must be satisfied. Because of this unique capability, the solid-state polymerization has been investigated from various research viewpoints. And also, solid-state polymerization is a solvent-free process and in future it will become more important as an environmentally friendly polymerization method.

Among the solid-state polymerizations of bulk monomer crystals, the polymerization can be divided into two classes: topotactic and topochemical polymerizations [74–79]. The former is the polymerization that provides a polymer with a specific crystal structure formed under control of the crystal

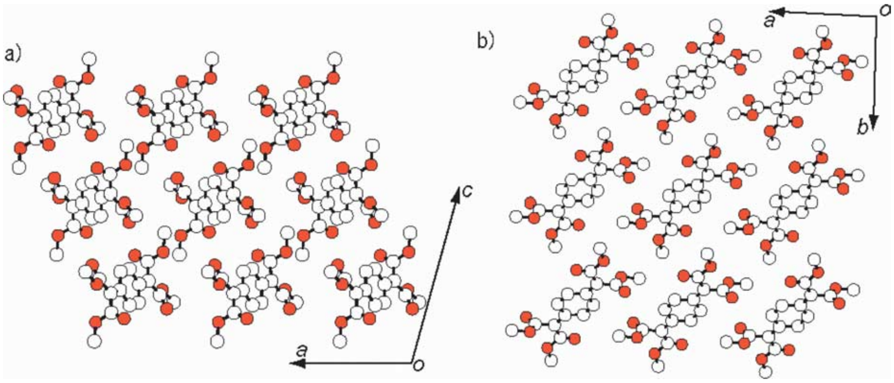
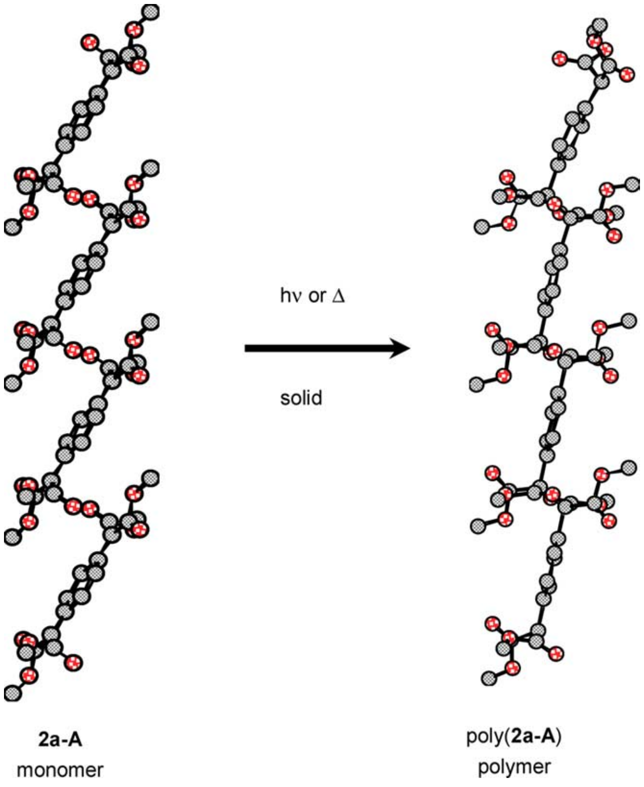


Fig. 6. Crystal structures of (a) **2a**–**A** viewed from the crystallographic *b* axis and (b) **2a**–**B** viewed from the crystallographic *c* axis. Hydrogen atoms are omitted for clarity. Open and filled circles represent carbon and oxygen atoms, respectively.

lattice of the monomers, and the latter is the polymerization that proceeds with no movement of the center of the gravity of the monomer molecule and only slight rotation of the monomer molecule around the gravity; that is, the crystallographic position and symmetry of the monomer crystals are retained in the resulting polymer crystals. Therefore, topochemical polymerization provides a promising method to obtain polymers where the primary structures such as regioselectivity and tacticity as well as higher order structures of chains such as ordering and crystallinity are completely controlled. However, in the late 1960s, only a limited number of monomers such as diacetylenic derivatives [74–79] and 2,5-distyrylpyradine and analogeous diolefines [80,81] have been reported to undergo topochemical polymerizations. No other monomers enable to polymerize in a topochemical manner have been found for a long time. Recently, successful topochemical polymerizations of trienes and triacetylenes [82–84] have been discovered by importing host-guest/cocrystal chemistry into the control of the topochemical polymerization and a unique polybutadiene ladder polymer has been produced. More recently, polymerizations of conjugated 1,3-diene monomers including some esters, amides, and ammonium salts of muconic and sorbic acids have been also found to proceed topochemically and the topochemical polymerization principles (5 Å rules) for diene monomers on the basis of their crystallographic data have been proposed [85–88]. As to a polymerization of electron-accepting substituted *p*-quinodimethanes in a solid state, it has been briefly reported that, on heating or on leaving **2a** to stand at room temperature in diffuse light, **2a** gives a completely insoluble pink product, not well characterized [5]. In addition to the fact, a series of our studies for electron-accepting substituted *p*-quinodimethanes in solution polymerizations, recent developments in topochemical polymerizations, especially 1,3-diene monomers and trienes and triacetylenes, and also dramatic developments of methods and apparatus for the crystal structure analysis provoke us to investigate a possibility of topochemical polymerizations in electron-accepting substituted *p*-quinodimethanes and substituted *p*-quinone methides, and, as a result, we have found topochemical polymerizations in some electron-accepting substituted *p*-quinodimethanes with ester groups [89–93].



Scheme 11.

3.1. Electron-accepting substituted p-quinodimethanes with same substituents

The solid-state polymerizations of 7,7,8,8-tetrakis(alkoxycarbonyl)quinodimethanes with methoxy (**2a**), ethoxy (**2b**), isopropoxy (**2c**), benzyloxy (**2d**), chloroethoxy (**2e**), and bromoethoxy (**2f**) as alkoxy groups as shown in Chart 1 were investigated [89,90]. Two crystal forms (prisms (**2a**–**A**) and

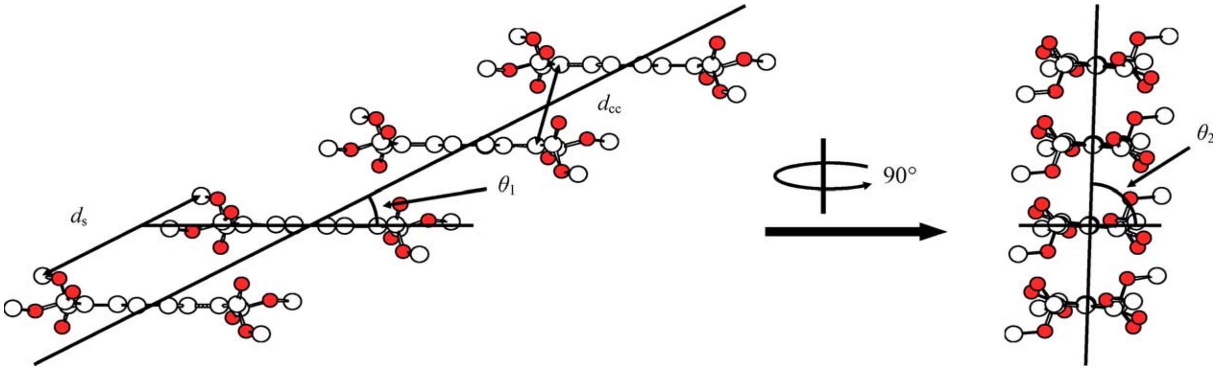


Fig. 7. Stacking model for the substituted *p*-quinodimethane in the crystals, and the definition of stacking parameters for the prediction of the topochemical polymerization reactivity. d_s is the stacking distance between the adjacent monomers in a column; d_{cc} is the distance between the reacting exomethylene carbons; θ_1 and θ_2 are the angles between the stacking axis and longer axis of the monomer molecule and the shorter axis of the molecule.

needles (**2a**–**B**), needles (**2c**–**A**) and plates (**2c**–**B**), prisms (**2e**–**A**) and plates (**2e**–**B**), and prisms (**2f**–**A**) and needles (**2f**–**B**)) depending upon recrystallization conditions have been obtained by recrystallizations of **2a**, **2c**, **2e**, and **2f** and all crystal structures of **2a**–**f** have been determined by X-ray crystallography. The formation of two crystal forms means a polymorphism phenomena in the crystallization of the substituted *p*-quinodimethanes and the difference in the packing manner between them is evident as shown in Fig. 6 for the **2a**. In the solid-state photopolymerization of these monomer crystals, **2a**–**A**, **2e**–**A**, and **2f**–**A** polymerized topochemically to give crystalline polymers, and in the solid-state thermal polymerizations, in addition to the three of **2a**–**A**, **2e**–**A**, and **2f**–**A**, **2e**–**B** and **2f**–**B** polymerize, but polymers formed from the **2e**–**B** and **2f**–**B** have been amorphous (Scheme 11). No thermal polymerization and photopolymerizations take place for **2a**–**B**, **2b**, **2c**–**A**, **2c**–**B**, and **2d**.

We have discussed the relationship of the solid-state polymerization reactivities with the molecular arrangements of the substituted *p*-quinodimethanes in the crystals on the basis of the stacking manners in the columnar structures by using structural parameters such as stacking distance (d_s), the distance between the reacting exomethylene carbon atoms (d_{cc}), the angles formed between the stacking axis and longer axis of the monomer molecule (θ_1) and the shorter axis of the monomer molecule (θ_2) as shown in Fig. 7. The parameters of **2a**–**f** are summarized in Table 6.

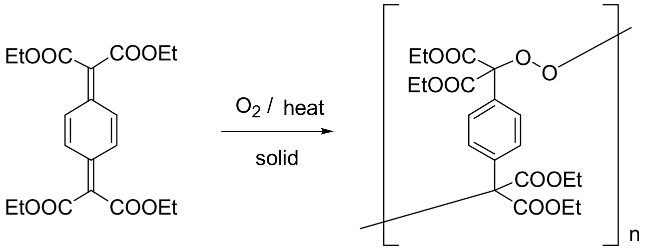
Table 6
Stacking parameters for crystals of **2a**–**f**

Monomer	θ_1 (deg)	θ_2 (deg)	d_s (Å)	d_{cc} (Å)
2a–**A**	30	89	7.6	3.9
2a–**B**	55	62	5.3	5.0
2b	90	90	3.4	4.3
2c–**A**	46	74	5.4	4.4
2c–**B**	49	41	8.9	6.8
2d	60	72	9.9	7.7
	43	47		
2e–**A**	32	83	7.6	4.2
2e–**B**	40	70	7.4	5.2
	50	52		
2f–**A**	33	89	7.0	3.8
2f–**B**	56	65	5.0	5.0

θ_1, θ_2, tilt angles of the molecular palne; d_{cc}, distance between the reacting exomethylene carbons; d_s, stacking distance.

The topochemically polymerizable monomers (**2a**–**A**, **2e**–**A**, and **2f**–**A**) are the crystal structures with parameters of $\theta_1 = 30$–$33°$, $\theta_2 = 83$–$89°$, $d_s = 7.0$–7.6 Å, and $d_{cc} = 3.8$–4.2 Å. Nearly face-to-face stacking with some offset along the longer molecular axis is requisite for crystalline state polymerizations of quinodimethane monomers. When monomer molecules are stacked in this specific distance in the crystals, reacting exomethylene carbons can be brought enough close ($d_{cc} = 3.8$–4.2 Å) only by the rotation of monomer without movement of a translational direction. It was pointed out that the d_s is close to that of a repeating distance (about 7.3 Å for poly(**2a**–**A**), calculated by molecular modeling, and 6.8 Å for poly(**2f**–**A**), determined by X-ray single crystal analysis) of the resulting crystalline polymer. This similarity of the unit lengths before and after polymerization affords high reactivities in crystalline state and polymers with high crystallinity and molecular weight.

The solid-state polymerization of **2b** does not proceed in vacuo with irradiation or heating, but **2b** copolymerizes with oxygen molecules in air to give an alternating copolymer (Scheme 12) [91,92]. ESR measurement has proved that the active spices in the solid-state polymerization of **2b** with molecular oxygen is to be a di(ethoxycarbonyl)benzyl radical, and also that the polymerization



2b

Scheme 12.

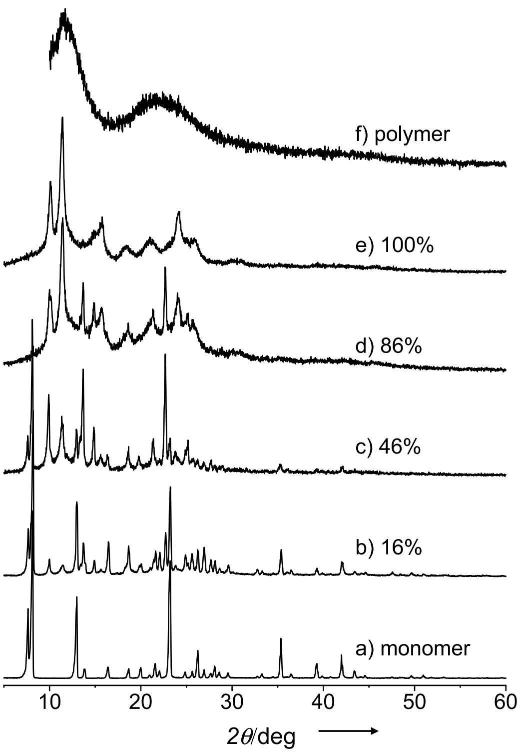


Fig. 8. Powder X-ray diffraction patterns of (a) monomer **2b**, (b) 16% conversion, (c) 46% conversion, (d) 86% conversion, (e) 100% conversion, and (f) reprecipitated polymer from chloroform–hexane.

reaction takes place at the disubstituted exomethylene carbon atoms and proceeds through a radical mechanism. The powder X-ray diffraction (XRD) measurements maintain the relatively sharp diffraction patterns even at the 100% conversion as shown in Fig. 8. After the reprecipitation treatment from chloroform–hexane, the peak of the powder XRD pattern changes broad, that is, the amorphous state (Fig. 8(f)). The changes observed in the powder XRD patterns indicate that the solid-state thermal polymerization of **2b** proceed under the influence of the crystal lattice to form the alternating copolymer with a highly ordered crystal structure. The packing mode of **2b** molecules in the crystals is quite different from those found in the topochemical polymerizations of substituted *p*-quinodimethanes. In the crystal structure of **2b** (Fig. 9), molecules construct an one-dimensional columnar structure by the stacking of the *p*-quinodimethane rings along the crystallographic *c* axis, and the stacking axes are nearly perpendicular to the molecular plane of the quinodimethane ring and molecules are piled up the next one with a rotational angle of 60°, and the distance between the reacting exomethylene carbon atoms in the column is 4.29 Å. No solid-state polymerizations of **2b** in vacuo are due to the lack of structural prerequisites for the topochemical polymerization. In contrast, the crystal packing is suit well for insertion of molecular oxygen diradicals between adjacent di(ethoxycarbonyl)benzyl radicals formed in the crystals, resulting in an alternating copolymer formation.

3.2. Electron-accepting substituted p-quinone methides with different substituents

The solid-state polymerizations of a series of 7-alkoxycarbonyl-7-cyano-1,4-benzoquinone methides (methoxy (**27a**), ethoxy (**27b**), isopropoxy (**27c**), propoxy (**27d**), butoxy (**27e**), and *sec*-butoxy (**27f**)) have been investigated [93]. In the solid-state thermal polymerization, **27a**, **27c**, **27d**, and **27e** polymerize to give glassy solids or a mass of crystals, but both of **27b** and **27f** do not. In the photopolymerization in the solid state, all monomer crystals except for **27a** polymerize to give corresponding polymers as needlelike solids, and the resulting polymers are the same polymer structures obtained in the melt or solution polymerizations in the presence of AIBN, where the polymerizations take place at a disubstituted exomethylene

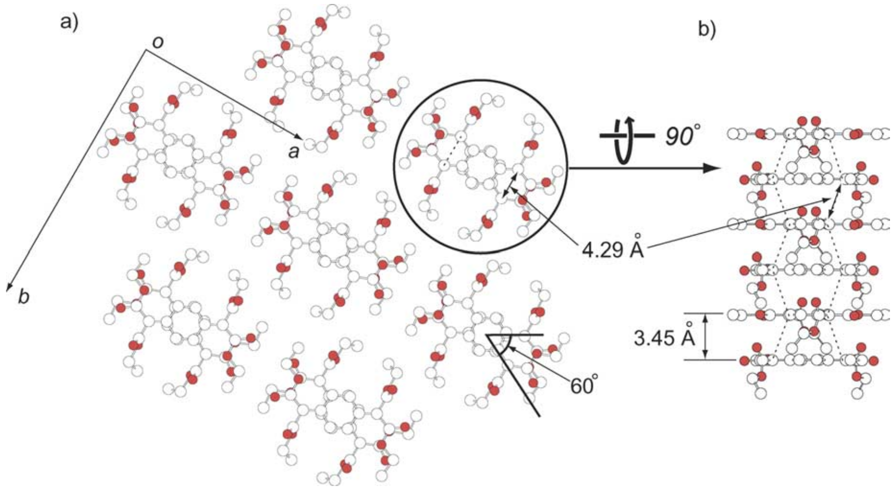


Fig. 9. Crystal structure of **2b** (a) viewed down the crystallographic *c* axis and (b) viewed down the crystallographic *b* axis. Hydrogen atoms are omitted for clarity. Open and filled circles represent carbon and oxygen atoms, respectively.

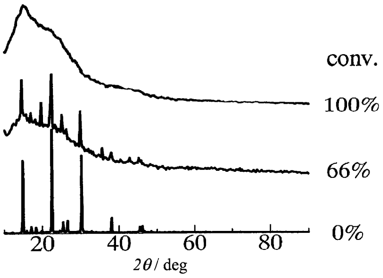


Fig. 10. Powder X-ray diffraction patterns of (a) monomer **27d**, (b) 66% conversion and (c) 100% conversion obtained by the solid-state photopolymerization of **27d**.

carbon atom and an exocarbonyl oxygen with a formation of the stable aromatic structure. The poly(**2d**) obtained as needlelike solids in the photopolymerization of the reactive **2d** becomes amorphous with a progress of the polymerization as shown in the powder XRD patterns at different conversions (Fig. 10). The amorphous polymer formation in the solid-state photopolymerization of **2d** is explained well by the difference in the stacking manners in the columnar structures between **2d** ($d_s = 4.8$ Å, $d_{co} = 6.3$ Å, $\theta_1 = 76°$, and $\theta_2 = 49°$) and topochemically polymerizable *p*-quinodimethanes ($\theta_1 =$ ca. 30°, $\theta_2 =$ ca. 90°, $d_s = 7.0$–7.6 Å, and $d_{cc} = 3.8$–4.0 Å) as shown in Fig. 11.

4. Conclusions

The solution and solid-state polymerizations of the isolable substituted *p*-quinodimethanes and *p*-quinone methides obtained by the substitution of hydrogen atoms at exocyclic positions with electron-withdrawing and/or electron-donating substituents have been investigated. The substituted *p*-quinodimethanes and *p*-quinone methides are more highly conjugative (reactive) in comparison to the conventional vinyl monomers, and their polymerization behaviors in the solution and in the solid state have been very unique ones, and, therefore, we believe that what we have found in the studies of polymerizations related to these substituted *p*-quinodimethanes and *p*-quinone methides may contribute to the further development of the polymer chemistry established by polymerizations of vinyl monomers. Only a limited number of the substituted *p*-quinodimethanes and *p*-quinone methides are isolable because they are highly reactive in essence, and, therefore, further understanding in their property is still insufficient. We expect that attempts to synthesize many members in quinonoid family including substituted quinone diimines and quinone methide imines in addition to substituted quinodimethanes and quinone methides and the studies of their properties would provide to a significant contribution to the development of the quinonoid chemistry.

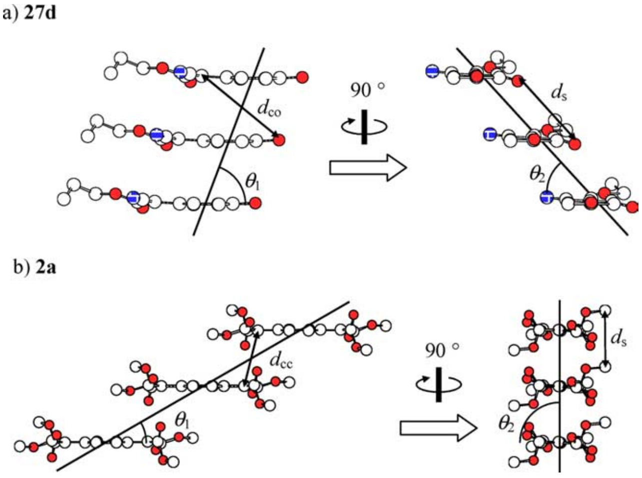


Fig. 11. Stacking models for **27d** and **2a**–**A** (prism) in the crystals, and the definition of stacking parameters for the prediction of the topochemical polymerization reactivity. d_s is the stacking distance between the adjacent monomers in a column; d_{co} and d_{cc} are the distance between the reacting exomethylene carbon and exocarbonyl oxygen or exomethylene carbon, respectively; θ_1 and θ_2 are the angles between the stacking axis and longer axis of the monomer molecule and the shorter axis of the molecule, respectively.

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